$(R_2PC_2H_4PR_2)Pd^0$−1-Alkyne Complexes

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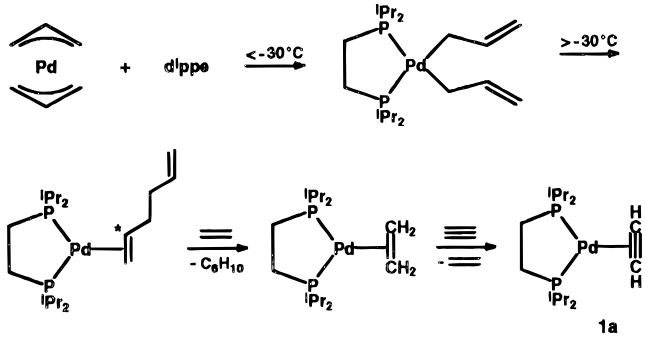
Displacement of the ethene ligand in (d^ippe)Pd(C_2H_4) (d^ippe = $^iPr_2PC_2H_4P^iPr_2$) by 1-alkynes RC≡CH affords the mononuclear complexes (d^ippe)Pd(RC≡CH) (R = Me (**2a**), Ph (**3a**), CO_2-Me (**4**), $SiMe_3$ (**5**)). The molecular structure of **3a** has been determined by X-ray crystallography. Mononuclear **2a** and **3a** have been reacted with stoichiometric amounts of (d^ippe)Pd(η^1-C_3H_5)$_2$ as a source for [(d^ippe)Pd^0] to yield the dinuclear derivatives {(d^ippe)-Pd}$_2$(μ-RC≡CH) (R = Me (**2b**), Ph (**3b**)). By the reaction of (d^ippe)Pd(C_2H_4) with difunctional vinylacetylene the mononuclear complex (d^ippe)Pd{(1,2-η^2)-RC≡CH} (R = CH=CH_2 (**6a**)) is formed, which is in equilibrium with isomeric (d^ippe)Pd{(3,4-η^2)-H_2C=CHC≡CH} (**6b**). Addition of [(d^ippe)Pd^0] to **6a,b** yields dinuclear {(d^ippe)Pd}$_2$(μ-RC≡CH) (R = CH=CH_2 (**6c**)). Reaction of (d^ippe)Pd(C_2H_4) with butadiyne affords (d^ippe)Pd(η^2-HC≡CC≡CH) (**7c**). From d^ippe, Pt(cod)$_2$, and C_4H_2 the Pt homologue has also been synthesized and thus, together with the already known Ni derivative, the series (d^ippe)M(η^2-HC≡CC≡CH) (M = Ni (**7a**), Pd (**7c**), Pt (**7f**)) is now complete. When **7c** and [(d^ippe)Pd^0] are combined, the dinuclear complex {(d^ippe)Pd}$_2$(μ-RC≡CH) (R = C≡CH (**7e**)) is formed in solution, whereas isomeric {(d^ippe)Pd}$_2${μ-(1,2-η^2):(3,4-η^2)-HC≡CC≡CH} (**7d**) is present in the solid state. The preparation of the Pd^0−1-alkyne complexes refutes the conventional wisdom that this type of compound is inherently unstable. By reaction of (d^ippe)Pd(C_2H_4) with internal alkynes C_2R_2 the complexes (d^ippe)Pd(RC≡CR) (R = Me (**8a**), Ph (**9**), CO_2Me (**10**), $SiMe_3$ (**11**)) have also been prepared. Combining **8a** with [(d^ippe)Pd^0] affords dinuclear {(d^ippe)Pd}$_2$(μ-MeC≡CMe) (**8b**). Finally, solution thermolysis of **2b** and **8b** gives rise to dinuclear alkyne-free Pd$_2$(d^ippe)$_2$ (**12**).

Introduction

Previous reports on the reaction of Pd^0 complexes with 1-alkynes give the impression that the preferred reaction path is oxidative addition to yield Pd^{II} alkynyl hydrides.[1] It appears, however, that the major obstacle in the synthesis of Pd^0−1-alkyne complexes has been the scarcity of appropriate starting complexes rather than an inherent instability of this type of complex. In this context we have recently reported on novel (R_2-$PC_2H_4PR_2$)Pd^0 alkene and ethyne complexes (R = ^{i}Pr, ^{t}Bu; alkene = C_2H_4, 1,5-hexadiene, 1,5-cyclooctadiene).[2] When Pd(η^3-C_3H_5)$_2$ and Pd(η^3-2-MeC_3H_4)$_2$ are reacted below −30 °C with bidentate $^iPr_2PC_2H_4P^iPr_2$ (d^ippe), the Pd^{II} η^1-allyl compounds (d^ippe)Pd(η^1-C_3H_5)$_2$[2] and (d^ippe)-Pd(η^1-2-MeC_3H_4)$_2$[3] are produced. Above −30 °C the allyl substituents couple with reduction of Pd^{II} to form various labile (d^ippe)Pd^0−1,5-hexadiene or −2,5-dimethyl-1,5-hexadiene complexes, which have in part been isolated. Addition of ethene furnishs uniformly the stable complex (d^ippe)Pd(C_2H_4), and by the reaction of the latter with ethyne mononuclear (d^ippe)Pd(C_2H_2) (**1a**) is obtained (Scheme 1). These complexes can also be prepared in one-pot reactions. Combination of **1a** with

Scheme 1



any of the aforementioned (d^ippe)Pd^{II,0} complexes produces dinuclear {(d^ippe)Pd}$_2$(μ-C_2H_2) (**1b**). Similar reactions carried out with $^tBu_2PC_2H_4P^tBu_2$ (d^tbpe) as the phosphane component afford (d^tbpe)Pd(C_2H_4), (d^tbpe)Pd(C_2H_2), and {(d^tbpe)Pd}$_2$(μ-C_2H_2).[2,4] Besides Pd(η^3-C_3H_5)$_2$ and Pd(η^3-2-MeC_3H_4)$_2$, the complexes (η^5-C_5H_5)Pd(η^3-C_3H_5) and (tmeda)PdMe$_2$ may serve alternatively as starting materials.

On the basis of the chemistry described above we set out to tackle the problem of the synthesis of Pd^0−1-alkyne complexes. We have confined the studies to d^ippe as an exemplary ligand to Pd because of the excellent properties it generally confers to products with respect to stability, solubility, and crystallizability. We report here on, to the best of our knowledge, the first

[⊗] Abstract published in *Advance ACS Abstracts,* August 15, 1997.

(1) (a) Chukhadzhyan, G. A.; Évoyan, Z. K.; Melkonyan, L. N. *Zh. Obshch. Khim.* **1975**, *45*, 1114; *J. Gen. Chem. USSR (Engl. Transl.)* **1975**, *45*, 1096. (b) Maitlis, P. M.; Espinet, P.; Russell, M. J. H. *Comprehensive Organometallic Chemistry*; Pergamon: Oxford, U.K., 1982; Vol. 6, p 254. (c) Davies, J. A. *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, U.K., 1995; Vol. 9, p 316.

(2) Krause, J.; Bonrath, W.; Pörschke, K.-R. *Organometallics* **1992**, *11*, 1158.

(3) Krause, J. Dissertation, Universität Düsseldorf, 1993.

(4) The molecular structures of (d^tbpe)Pd(HC≡CH) (C≡C = 1.20(1) Å) and {(d^tbpe)Pd}$_2$(μ-HC≡CH) (C≡C = 1.28(1) Å) have been determined.[3] Goddard, R.; Krause, J.; Pörschke, K.-R. Unpublished results.

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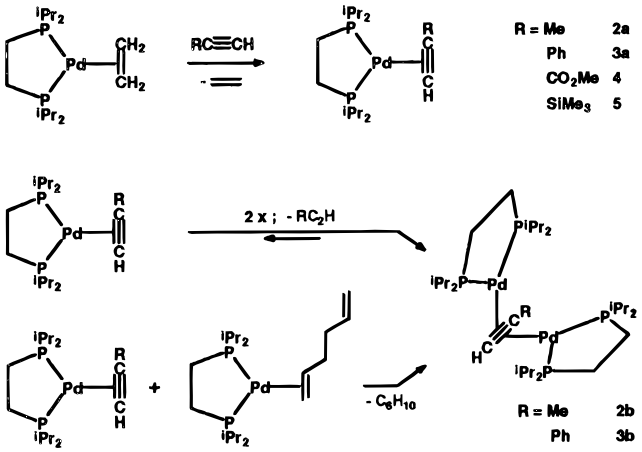
Scheme 2



isolated[5] Pd^0−1-alkyne complexes and also some new Pd^0 complexes with internal alkynes.[6] While related Ni(0)−1-alkyne complexes[7] are still scarce, the group of Pt(0)−1-alkyne complexes[8] is quite broad.

Results

(d^ippe)Pd^0 Complexes with MeC≡CH, PhC≡CH, MeO_2CC≡CH, and Me_3SiC≡CH (2−5). While the methyl group in propyne is electron-donating ("nonactivated alkyne"), the phenyl or ester substituents in phenylacetylene and propiolic acid methyl ester are electron-withdrawing ("activated alkyne"), whereas the electronic effect of the Me_3Si substituent in (trimethylsilyl)acetylene is a priori difficult to assess. When (d^ippe)Pd(C_2H_4) is reacted with an excess of these 1-alkynes in pentane or diethyl ether at ≤0 °C, the ethene ligand is readily displaced and, upon cooling to −78 °C, the mononuclear (d^ippe)Pd^0−1-alkyne complexes **2a**, **3a**, **4**, and **5** are obtained (Scheme 2). Although the complexes can also be prepared by one-pot reactions of any of the Pd^{II} complexes mentioned in the Introduction with d^ippe and the 1-alkyne (cf. Scheme 1), the reaction of isolated (d^ippe)Pd(C_2H_4) with 1-alkyne appears to be favorable.

The mononuclear complexes **4** and **5** are stable in solution at ambient temperature. When solutions of complexes **2a** and **3a** are warmed to 20 °C, additional signals arise in the NMR spectra which are attributed to the dinuclear derivatives {(d^ippe)Pd}$_2$(μ-RC≡CH) (R = Me (**2b**), Ph (**3b**)). Complex **2b** has been obtained in pure form by depleting propyne from the ethereal solution of **2a** under vacuum. Furthermore, complexes **2b** and **3b** have been synthesized by reacting **2a** and **3a** with an equimolar amount of (d^ippe)Pd(η^1-C_3H_5)$_2$. The latter thermolyzes into (d^ippe)Pd(η^2-C_6H_{10}) and thus serves as a source for [(d^ippe)Pd^0]. (d^ippe)Pd(η^2-C_6H_{10}) is more reactive than (d^ippe)Pd(C_2H_4), for which the coupling reactions with (d^ippe)Pd(RC≡CH) are incomplete. It appears without doubt that also **4** and **5** will react with [(d^ippe)Pd^0] to form the corresponding dinuclear complexes.

The colorless or faintly colored crystalline complexes are isolated in 80−90% yield. The melting points of the mononuclear complexes are relatively low (30−81 °C), while those of the dinuclear complexes are somewhat higher (70−110 °C). When a THF-d_8 solution of **2a,b** is kept at 20 °C for several days, a slow decomposition proceeds to afford a mixture of products. Of these, the dinuclear alkyne-free complex **12** (see below) has been identified by its characteristic high-field ^{31}P NMR singlet (δ_P 33.7).

Although the mononuclear complexes **4** and **5** are stable in solution when pure, they are destabilized by additional 1-alkyne. When to a solution (THF-d_8, 20 °C) of the mononuclear complexes **2a**, **3a**, **4**, and **5** about 4 equiv of the corresponding 1-alkyne is added, for **3a** and phenylacetylene a slight decomposition is observed after 1 day. However, for **5** and (trimethylsilyl)acetylene some decomposition is observable already after 1 h, and the situation is similar for **2a** and added propyne. For **4** and propiolic acid methyl ester decomposition is the most rapid and proceeds largely within 1 h. Thus, the following qualitative sequence of increased destabilization (increased reactivity) has been established:

3a/HC≡CPh < **5**/HC≡C$SiMe_3$ ≈ **2a**/HC≡CMe < **4**/HC≡CCO_2Me

It is deemed that decomposition is initiated by the oxidative addition of a 1-alkyne C−H bond to (d^ippe)-Pd^0(1-alkyne), giving rise to a $Pd^{II/IV}$ alkynyl hydride intermediate. Further reaction with 1-alkyne may lead to 1-alkyne oligomerization.[9] For the given [(d^ippe)Pd^0] system the formation of various oligomers is indicated by the ^{1}H NMR spectra. Of these oligomers the *cyclic* trimer[10] 1,3,5-C_6H_3($COOMe$)$_3$[11] has been identified. No NMR signals for $Pd^{II/IV}$ alkynyl hydride species have been observed.

(5) For IR spectroscopically characterized species obtained by co-condensation of Pd atoms and 1-alkynes, see: Zoellner, R. W.; Klabunde, K. J. *Chem. Rev.* **1984**, *84*, 545 and literature cited therein.

(6) (a) Schager, F. Diplomarbeit, Universität Düsseldorf, 1995. (b) Schager, F.; Pörschke, K.-R. *GECOM-CONCOORD 1995*, University of Rennes, May 28−June 1, 1995; St Jacut de la Mer, France. (c) Schager, F. Planned Dissertation (1997).

(7) (a) (bpy)Ni(CO)$_2$(PhC≡CH) (unknown structure): Herrera, A.; Hoberg, H.; Mynott, R. *J. Organomet. Chem.* **1981**, *222*, 331. (b) (Me_3P)$_2$Ni(PhC≡CH): Pörschke, K.-R.; Mynott, R.; Angermund, K.; Krüger, C. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1985**, *40*, 199. (c) (Ph_3P)$_2$Ni(PhC≡CH): Pörschke, K.-R.; Tsay, Y.-H.; Krüger, C. *Angew. Chem.* **1985**, *97*, 334; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 323. Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103. Bartik, T.; Happ, B.; Iglewsky, M.; Bandmann, H.; Boese, R.; Heimbach, P.; Hoffmann, T.; Wenschuh, E. *Organometallics* **1992**, *11*, 1235. (d) Chetcuti, M. J. *Comprehensive Organometallic Chemistry II*; Pergamon: Oxford, U.K., 1995; Vol. 9, p 129.

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(9) For examples of Pd-catalyzed oligo- or polymerization of terminal alkynes, see: (a) Odaira, Y.; Hara, M.; Tsutsumi, S. *Technol. Rep. Osaka Univ.* **1965**, *16*, 325; *Chem. Abstr.* **1966**, *65*, 10670f. (b) Maitlis, P. M. *Acc. Chem. Res.* **1976**, *9*, 93 and references cited therein. (c) Simionescu, C. I.; Percec, V.; Dumitrescu, S. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2497. (d) Sabourin, E. T. *J. Mol. Catal.* **1984**, *26*, 363. (e) Ishikawa, M.; Ohshita, J.; Ito, Y.; Minato, A. *J. Organomet. Chem.* **1988**, *346*, C58. (f) Dzhemilev, U. M.; Khusnutdinov, R. I.; Shchadneva, N. A.; Nefedov, O. M.; Tolstikov, G. A. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1989**, 2360; *Bull. Acad. Sci. USSR, Div. Chem. Sci. (Engl. Transl.)* **1990**, 2171. (g) Trost, B. M.; Sorum, M. T.; Chan, C.; Harms, A. E.; Rühter, G. *J. Am. Chem. Soc.* **1997**, *119*, 698.

(10) It will be shown in a separate paper that [(iPr$_3$P)Pd^0] regio- and stereospecifically catalyzes the oligomerization of 1-alkynes to form *linear* trimers.[3] Krause, J.; Schager, F.; Pörschke, K.-R. 32nd International Conference on Coordination Chemistry, Santiago, Chile, Aug 24−29, 1997.

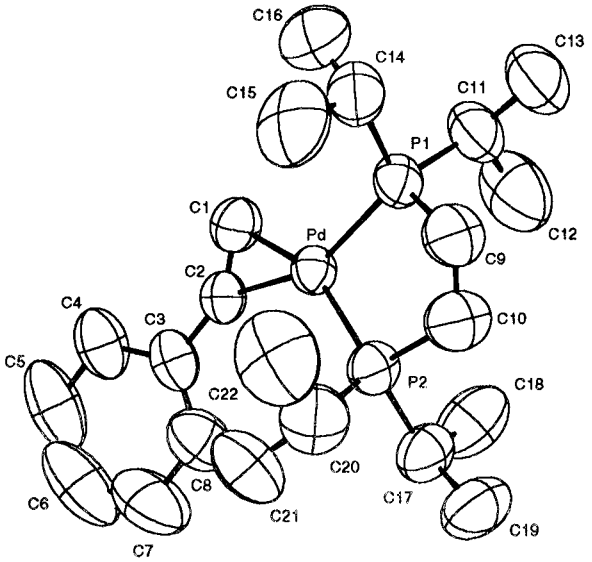

Figure 1. Molecular structure of complex **3a**. Selected bond distances (Å): Pd−P1 = 2.294(1), Pd−P2 = 2.301(1), Pd−C1 = 2.028(5), Pd−C2 = 2.062(4), C1−C2 = 1.246(7). Selected bond and dihedral angles (deg): P1−Pd−P2 = 87.2(1), P1−Pd−C1 = 116.6(1), P1−Pd−C2 = 152.1(1), P2−Pd−C1 = 156.2(1), P2−Pd−C2 = 120.8(1), C1−C2−C3 = 143.8(5), C2−C1−H1 = 149(3), Pd,P1,P2/Pd,C1,C2 = 0.6, Pd,C1,C2/(C3−C8) = 20.2.

Molecular Structure of (d^ippe)Pd(PhC≡CH) (3a). The molecular structure of **3a** (Figure 1) has been determined by X-ray crystallography. Due to the monosubstitution of the alkyne ligand and the nonplanar (d^ippe)Pd chelate ring, the molecular point symmetry is C_1. The (d^ippe)Pd fragment of **3a** displays features similar to those in other (d^ippe)Pd complexes.[12,13] Thus, the P1−Pd−P2 angle of 87.2(1)° and the P−Pd bond lengths of 2.294(1) and 2.301(1) Å compare very well with the mean values (angle 87.17° and bond length 2.304 Å) for the compounds in refs 12 and 13. However, the "bite angle" P1−Pd−P2 in **3a** is significantly smaller than for the Pd^0−alkyne complexes with monodentate phosphanes $(Ph_3P)_2Pd(MeO_2CC{\equiv}CCO_2Me)$[14a] (**A,** 107°) and $\{(c\text{-}C_6H_{11})_3P\}_2Pd(F_3CC{\equiv}CCF_3)$[14b] (**B**, 111°), resulting in a higher donor strength for the d^ippe ligand. Consequently, the Pd−P bond length is distinctly shorter than for **A** (2.33 Å (mean)) and **B** (2.36 Å (mean)), and the coordination geometry at the *TP*-3 Pd^0 center in **3a** is exactly planar (Pd,P1,P2/Pd,C1,C2 0.6°), whereas for **A** (10°) and **B** (3°) larger distortions from planarity are observed. In **3a** the coordinated C≡C bond C1−C2 (1.246(7) Å) is relatively short (uncoordinated C≡C: 1.18−1.20 Å), while the length of Pd−C (Pd−C1 = 2.028(5), Pd−C2 = 2.062(4) Å) is of the same magnitude as for **A** (C≡C = 1.28 Å; Pd−C = 2.06 Å (mean)) and **B** (C≡C = 1.27 Å; Pd−C = 2.05 Å (mean)). In particular, the coordinated C≡C bond is less elongated than for the corresponding Ni^0 and Pt^0 complexes (d^ippe)Ni(HC≡CH) (1.287(7) Å) and (d^ippe)Pt(HC≡CH) (1.37(3) Å),[15] in agreement with a relatively weak back-bonding strength of Pd^0. The deviation of the phenyl substituent from collinearity with the alkyne C atoms in **3a** (36.2°) is of intermediate magnitude (**A**, 35°; **B**, 44°). In **3a** the plane of the phenyl group is tilted toward the Pd coordination plane by 20°, which may be caused by crystal-packing effects.

Spectroscopic Properties of 2−5. Complexes **2**−**5** have been characterized by their MS, IR, and ^{1}H, ^{13}C, and ^{31}P NMR spectra. In the EI mass spectra the mononuclear Pd^0−1-alkyne complexes **2a**, **3a**, **4**, and **5** (vaporization temperature 20−50 °C) display the molecular ions which fragment by cleavage of the 1-alkyne ligands to afford $[(d^i\text{ppe})Pd]^+$ (*m*/*e* 368) as common base ion.[16] With respect to the dinuclear alkyne complexes **2b** and **3b** (120 °C), the molecular ion has been observed only for the phenylacetylene derivative **3b**, but both complexes give rise to the dinuclear *alkyne-free* ion $[Pd_2(d^i\text{ppe})_2]^+$ (**12**$^+$, *m*/*e* 736). The latter monomerizes into $[(d^i\text{ppe})Pd]^+$, which represents the base ion for **2b**.

In the IR spectra (Table 1) of the mononuclear (d^ippe)-Pd^0−1-alkyne complexes **2a, 3a**, **4**, and **5** the 1-alkyne C−H stretching band is shifted from about 3300 ± 30 cm^{-1} for the free alkyne to 3085 ± 25 cm^{-1}, corresponding to a coordination shift of $\Delta\nu$(C−H) = 210 ± 25 cm^{-1}. For **2a**, **3a**, and **4** the C≡C stretching bands are shifted to 1735 ± 25 cm^{-1}, corresponding to $\Delta\nu$(C≡C) = 395 ± 15 cm^{-1}. For **4**, of course, the observed value $\Delta\nu$(C≡C) may be somewhat influenced by the occurrence of vibrational coupling of the C≡C and C═O groups (ν(C═O) 1667 cm^{-1}) in the coordinated alkyne, different from the situation in the free alkyne. Significantly smaller values $\Delta\nu$(C≡C) are observed for **1a** (355 cm^{-1}) and **5** (326 cm^{-1}), for which ν(C≡C) values for the uncoordinated alkynes are particularly low.

When the alkyne ligand of the Pd^0−1-alkyne complexes is coordinated to a second (d^ippe)Pd^0 fragment, additional "complementary" coordination shifts to lower wavenumbers are observed, resulting uniformly for **1b**−**3b** in an absorption band ν(C−H) 3060 ± 5 cm^{-1} and in a total C≡C bond complexation shift $\Delta\nu$(C≡C) 600 ± 20 cm^{-1}. Although a direct comparison of Pd^0−1-alkyne and corresponding Ni^0−1-alkyne[7] and Pt^0−1-alkyne[8] complex IR data would only be meaningful if the same phosphane ligand (d^ippe) was applied, it is evident from a qualitative examination of the available data that the coordination shifts $\Delta\nu$(C−H) and $\Delta\nu$(C≡C) are distinctly smaller for the Pd^0−1-alkyne complexes than for the Ni^0− and Pt^0−1-alkyne derivatives.

In the ^{1}H and ^{13}C NMR spectra (Table 2) of the mononuclear complexes **1a**−**3a**, **4**, and **5** the alkyne ≡CH and −C≡ resonances are shifted by $\Delta\delta_H$ = 3.9−4.7 ppm and $\Delta\delta_C$ = 28−45 ppm to low field as compared to the uncoordinated alkyne (for **5**, $\Delta\delta_C$(SiC≡) = 21.2 ppm appears to be exceptionally small). When the dinuclear derivatives **1b**−**3b** are formed from **1a**−**3a**,

(11) The Aldrich Library of ^{13}C and ^{1}H FT NMR Spectra; 1st ed.; Aldrich Chemical: Milwaukee, WI 1993; p 1282 (spectrum for 11,598−3).

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(14) (a) McGinnety, J. A. *J. Chem. Soc., Dalton Trans.* **1974**, 1038. (b) Farrar, D. H.; Payne, N. C. *J. Organomet. Chem.* **1981**, *220*, 239.

(15) (a) Haack, K.-J. Dissertation, Universität Düsseldorf, 1994. (b) Krüger, C.; Goddard, R. Unpublished results.

(16) In the EI mass spectra the fragmentation of (d^ippe)Pd^0− and (d^tbpe)Pd^0−alkene/alkyne complexes is initiated by loss of the alkene or alkyne ligand to produce the Pd^I radical ions $[(d^i\text{ppe})Pd]^+$ and $[(d_t\text{-bpe})Pd]^+$. The Pd^I ions fragment by radical substituent cleavage to afford the Pd^{II} ions $[(^i\text{Pr}_2PC_2H_4P^i\text{Pr})Pd]^+$ and $[(^t\text{Bu}_2PC_2H_4P^t\text{Bu})Pd]^+$, which successively eliminate propene or 2-methylpropene to yield $[(H_2PC_2H_4PH)Pd]^+$. In contrast, for $[(d^i\text{ppe})M]^+$ and $[(d^t\text{bpe})M]^+$ (M = Ni, Pt) alkene elimination proceeds with preservation of the M^I radical ion character.

Table 1. Selected IR (Raman) Data for the Alkyne Ligands of the Mono- and Dinuclear (d^{i}ppe)Pd^0−Alkyne Complexes 1−6 and 8−11

	ν(C−H) (cm^{-1})			ν(C≡C) (cm^{-1})		
	free alkyne	coord alkyne	$\Delta\nu$	free alkyne	coord alkyne	$\Delta\nu$
1a	3374 (Ra) sym[a]	3125 sym	249	1974 (Ra)[a]	1619	355
	3289 asym[a]	3085 asym	204			
1b		3065 sym[b]	309		1370	604
2a	3344/23[c]	3107	227	2152/27[c]	1756	384
2b		3058	276		1528	612
3a	3291	3062	229	2110	1720	390
3b		3055	236		1524	586
4	3273	3087	186	2127	1718[d]	409
5	3293	3099	194	2036	1710	326
6a	3298	3087	211	2105	1717	388
6c		3080[e]	(218)		1498	607
8a				2240 (Ra)	1862	378
8b					1618	622
9				2223 (Ra)	1827	396
10				2248 (Ra)	1811[d]	437
11				2110 (Ra)	1771	339

[a] Gaseous ethyne. [b] Very weak band; hard to detect. [c] Gaseous propyne; P and R branches. [d] Band involves C−C and C−O stretchings. [e] Assignment uncertain due to olefinic C−H bands occurring in the same region.

Table 2. Selected ^{1}H, ^{13}C, and ^{31}P NMR Data for the Mono- and Dinuclear (d^{i}ppe)Pd^0−Alkyne Complexes 1−6 and 8−11[a]

	δ_H(≡CH)			δ_C(−C≡)			δ_C(≡CH)					
	coord alkyne	free alkyne	$\Delta\delta_H$	coord alkyne	free alkyne	$\Delta\delta_C$	coord alkyne	free alkyne	$\Delta\delta_C$	^1J(CH)[d] coord alkyne	δ_P	^2J(PP)[d]
1a	6.91	2.40	4.51				106.6	71.9	34.7	211	69.5	
1b	5.75		3.35				67.7		−4.2	200	59.9	
2a[b]	6.21	1.80	4.41	116.0	80.0	36.0	96.4	68.3	28.1	212	68.0, 67.8	45
2b[b]	5.44		3.64	85.4		5.4	67.7		−0.6	196	59.3, 57.3[e]	
3a	7.36	3.44	3.92	129.4	84.9	44.5	107.7	79.2	28.5	211	70.6, 67.5	34
3b	5.78		2.34	92.2		7.3	66.6		−12.6	198	61.3, 55.1[e]	
4	7.34	3.49	3.85	117.5	75.4	42.1	112.2	76.6	35.6	210	74.2, 71.3	19
5	7.26	2.58	4.68	116.3	95.1	21.2	121.3	89.8	31.5	212	68.5, 65.9	46
6a[c]	7.13	3.30	3.83	123.5	82.8	40.7	109.8	79.4	30.4		69.9, 68.4	32
6c[c]	5.49		2.19	88.5		5.7	65.5		−13.9		61.1, 57.7[e]	
8a				106.6	74.9	31.7					67.1[c]	
8b[b]				84.9		10.0					58.0	
9				126.1	90.1	36.0					67.5	
10				122.7	74.9	47.8					75.7	
11				134.7	114.0	20.7					63.4	

[a] Solvent THF-d_8, temperature 27 °C. [b] Temperature −30 °C. [c] Temperature −80 °C. [d] Coupling constant in hertz. [e] Approximate values of a nonsimulated AA′BB′ spin system.

an opposite shift to high field is observed, so that the coordination chemical shifts[17] $\Delta\delta_H$ and $\Delta\delta_C$ are now markedly smaller and even become negative for the unsubstituted alkyne C atom. For mononuclear **2a**, **3a**, **4**, and **5** ABX spin systems are observed for the ≡C*H* (A, B = ^{31}P; X = ^{1}H) and the ≡*C*H and −*C*≡ resonances (A, B = ^{31}P; X = ^{13}C), and for dinuclear **2b** and **3b** the corresponding nuclei give rise to well-resolved A_2B_2X multiplets ("triplet of triplets"). In agreement with this, the ^{31}P NMR spectra display sharp AB (**2a**, **3a**, **4**, **5**) or AA′BB′ (**2b**, **3b**) multiplets. When the solution of **2a,b** is warmed from −30 to 27 °C, the HC≡C*C*H$_3$ ligand resonances are *slightly* broadened but the multiplet patterns are maintained.[18] It follows from these features that for both mono- and dinuclear complexes the coordination of the 1-alkyne to the (d^{i}ppe)Pd^0 moieties can be considered to be rigid on the NMR time scale (C_s symmetry). For **2a,b** the spectra indicate a "starting slow rotation" at ambient temperature.

With regard to the coupling constant ^1J(CH) of the 1-alkyne ligand, it has been found that it is lowered from about 250 Hz for the uncoordinated 1-alkyne to about 211 Hz in the mononuclear complexes (**1a**, **2a**, **3a**, **4**, **5**) and to ≤200 Hz in the dinuclear derivatives (**1b**, **2b**, **3b**).

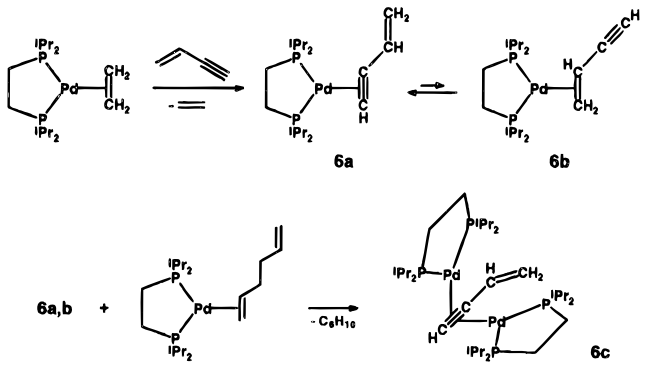
(d^{i}ppe)Pd^0−Vinylacetylene Complexes (6a−c). After we had established that 1-alkynes indeed form stable complexes with Pd^0, it was of further interest to explore how the reactivity of the terminal C≡C bond is influenced by conjugation to a C=C or C≡C bond. For this purpose we studied [(d^{i}ppe)Pd^0] coordination compounds with vinylacetylene and butadiyne (see below).

When vinylacetylene is added to a pentane solution of (d^{i}ppe)Pd(C$_2$H$_4$) at −78 °C, colorless crystals of **6a,b** precipitate in almost quantitative yield. According to the IR spectrum this precipitate consists of a roughly 4:1 mixture of complex isomers in which the enyne ligand is coordinated by either the C≡C bond (**6a**) or the C=C bond (**6b**) to Pd^0 (Scheme 3). Thus, the major isomer **6a** displays absorption bands (Table 1) at 3087 and 1717 cm^{-1} for the η^2-C≡CH moiety and further

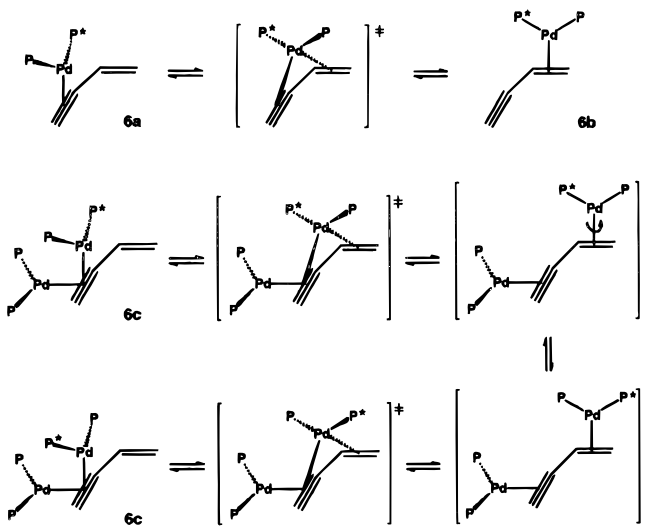
(17) The ^{1}H and ^{13}C coordination chemical shift, i.e., the change in chemical shift which the alkyne experiences upon coordination to a metal center, is defined by $\Delta\delta = \delta_{ligand} - \delta_{free\ alkyne}$. Thus, typical alkyne coordination shifts to lower field are positive, whereas those to higher field are negative. Jolly, P. W.; Mynott, R. *Adv. Organomet. Chem.* **1981**, *19*, 257.

(18) The ^{31}P AB signals of **2a** coalesce at 27 °C due to the very small difference in chemical shifts.

Scheme 3



Scheme 4



bands at 3010 and 1582 cm^{-1} for the uncoordinated $CH{=}CH_2$ function (cf. vinylacetylene: 3106, 3016 (=C−H) and 1599 (C=C) cm^{-1}), whereas absorption bands at 3317 and 2068 cm^{-1} are attributed to the uncoordinated C≡CH moiety of the η^2-$CH{=}CH_2$ isomer **6b**. The same mixture of isomers is isolated when the reaction is carried out in diethyl ether at 20 °C and the product is crystallized at −30 or −78 °C. The η^2-C≡CH isomer **6a** is considered to be thermodynamically slightly more stable than the η^2-$CH{=}CH_2$ isomer **6b**. The presence of **6b** in the solid is deemed to result from a crystallization effect. According to the ^1H and ^{31}P NMR spectra, a solution (THF-d_8) of **6a,b** at −80 °C contains almost exclusively **6a** but an increasing amount of **6b** (40%) is formed when the solution is warmed to ambient temperature. Complex **6a,b** is only moderately soluble in THF at low temperature and is even less so in diethyl ether. It slowly decomposes as a solid (mp 76 °C) at 20 °C and is somewhat less stable in solution. By solution thermolysis (20 °C) some dinuclear **6c** but no **12** (see below) is formed. In the EI mass spectrum **6a,b** exhibit a molecular ion (*m/e* 420, 6%) which fragments by cleavage of the enyne ligand to afford the base ion $[(d^ippe)Pd]^+$ (*m/e* 368).

In the solution ^1H NMR spectrum (−80 °C) the acetylenic proton of **6a** gives rise to a low-field doublet of doublets (δ_H 7.13) due to different couplings $^3J(PH)_{trans}$ and $^3J(PH)_{cis}$. Both the chemical shift and the multiplet structure are typical for $(d^ippe)Pd^0$−1-alkyne complexes (Table 2). Concerning the vinyl protons, the signal of $CH_2{=}CH-$ is also at relatively low field (δ_H 6.97) but for the terminal protons (δ_H 5.40 (=CHH_Z), 5.25 (=CH_EH)) the changes in the chemical shift are less pronounced as compared to uncoordinated vinylacetylene (δ_H 3.30 (HC≡), 5.81 (−CH=), 5.65 (=CHH_Z), 5.50 (=CH_EH)). Similarly, the ^{13}C NMR signals for the coordinated C≡C bond at δ_C 123.5 (≡C−) and 109.8 (≡CH) (Table 2) are at significantly lower field from the corresponding signals of uncoordinated vinylacetylene (δ_C 82.8 (≡C−), 79.4 (≡CH)) and display distinctly different couplings $^2J(PC)_{trans}$ (ca. 65 Hz) and $^2J(PC)_{cis}$ (ca. 4 Hz), whereas the vinyl signals at δ_C 128.1 (−CH=) and 120.7 (=CH_2) are close to those of uncoordinated vinylacetylene (δ_C 117.5 (−CH=), 128.4 (=CH_2)). Furthermore, the d^ippe ligand ^1H and ^{13}C signals of **6a** indicate C_s symmetry of the complex (the mirror plane passing through Pd, both P atoms, and the vinylacetylene skeleton), in agreement with a coordinated C≡C bond, whereas for **6b** (coordinated unsymmetrical C=C bond) C_1 symmetry is expected.

In contrast, for the vinylacetylene ligand in **6b** (20 °C) all ^1H resonances are shifted to higher field as compared to uncoordinated vinylacetylene. Most strongly affected are the protons =CH− (δ_H 3.12) and $=CH_ZH_E$ (δ_H 2.49, 2.36) of the coordinated vinyl group. The ≡CH resonance (δ_H 2.63) is still in the range expected for uncoordinated alkynes, and the moderate high-field shift is explained by a weakened conjugation between C≡C and the (now coordinated) C=C bond. An assignment of the d^ippe resonances of **6b** is difficult to achieve because of the expected low symmetry and the presence of the isomer mixture.

In the ^{31}P NMR spectrum (27 °C) the isomers **6a** and **6b** display sharp AB spin systems. For **6b** the signals are at somewhat higher field and $^2J(PP)$ = 43 Hz is larger than for **6a** (32 Hz), indicating that in **6b** more charge remains at the Pd atom due to a weaker electron withdrawal induced by the vinyl group as compared to that by the alkyne moiety in **6a**.

It follows from the NMR spectra that in the complexes neither the alkyne ligand (**6a**) nor the vinyl ligand (**6b**) rotates rapidly about the bond axis to $[(d^ippe)Pd^0]$. Furthermore, the isomerization reaction **6a** ⇌ **6b** (Scheme 3) is slow at 20 °C on the NMR time scale and no exchange of **6a,b** with uncoordinated vinylacetylene has been detected (^1H NMR). In compliance with other exchange reactions of oligofunctional alkenes (butadiene, isoprene,[19] *p*-benzoquinone, cyclooctadiene, 1,5-hexadiene,[2] stannacyclopentadiene,[12b] cyclooctatetraene[6c]) at *TP*-3 Pd^0 we suppose that the slow isomerization **6a** ⇌ **6b** proceeds by an *intramolecular* mechanism via a *T*-4 Pd^0 transition state (Scheme 4).

The fact that in mononuclear **6a,b** the $[(d^ippe)Pd^0]$ fragment is coordinated to the C≡C bond (**6a**) *or* the C=C bond (**6b**) led to the expectation that in a dinuclear derivative (**6c**) the $[(d^ippe)Pd^0]$ fragments were coordinated to both C≡C *and* C=C bonds. This is, however, not true. When the ethereal solution of **6a,b** is treated at 0 °C with an equimolar amount of $(d^ippe)Pd(\eta^2$-$C_6H_{10})$, generated in situ from $(d^ippe)Pd(\eta^1$-$C_3H_5)_2$, orange crystals of the dinuclear vinylacetylene complex **6c** are obtained (−78 °C) (Scheme 3). As follows from the MS, IR, and NMR data, the $[(d^ippe)Pd^0]$ fragments in **6c** are coordinated exclusively to the C≡C bond.

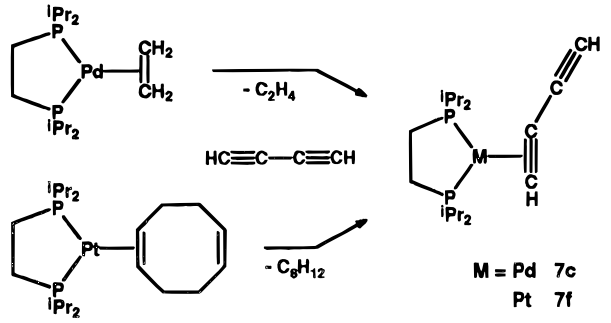
(19) (a) Benn, R.; Jolly, P. W.; Joswig, T.; Mynott, R.; Schick, K.-P. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1986**, *41*, 680. (b) Topalovic, I. Dissertation, Universität Siegen, 1990. (c) Benn, R.; Betz, P.; Goddard, R.; Jolly, P. W.; Kokel, N.; Krüger, C.; Topalovic, I. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1991**, *46*, 1395.

The mass spectrum of **6c** displays M^+, the alkyne-free ion $[Pd_2(d^ippe)_2]^+$ (**12**$^+$, see below) typical for $\{(d^ippe)Pd\}_2(\mu$-alkyne) complexes, and the base ion $[(d^ippe)Pd]^+$. In the IR spectrum a band at 1498 cm^{-1} can be assigned to the bridging 1-alkyne ligand, whereas ν(C═C) 1600 cm^{-1} corresponds to the uncoordinated vinyl group. In the ^{1}H NMR spectrum (−80 °C) of **6c** the ≡CH resonance at δ_H 5.49 represents a triplet of triplets due to the couplings to two pairs of formally *trans*- and *cis*-positioned P atoms. The signal of CH_2═C*H*− is shifted further to low field (δ_H 7.16), but the signals of the terminal vinyl protons (δ_H 4.79 (═CH*H*$_Z$), 4.32 (═C*H*$_E$H)) are at relatively high field (cf. **6a**). Correspondingly, the ^{13}C resonances of ≡C− (δ_C 88.5) and ≡CH (δ_C 65.5) are of the magnitude (cf. Table 2) and display phosphorus couplings as expected for a μ-alkyne ligand. For the uncoordinated vinyl group the −CH═ signal is shifted further to low field (δ_C 142.7) and the ═CH_2 signal is shifted further to high field (δ_C 104.1) in the following sequence: uncoordinated vinylacetylene → **6a** → **6c**. The high-field location and the AA′BB′ multiplet of the ^{31}P signals are also indicative of a $\{(d^ippe)Pd\}_2(\mu$-1-alkyne) complex.

At 27 °C the vinylacetylene ^{1}H signals and the ^{31}P NMR signals are significantly broadened, indicating a dynamic structure of **6c**. The structural dynamics of **6c** are *intramolecular* and are not due to cleavage of one $[(d^ippe)Pd^0]$ fragment, as evidenced by the fact that for a mixture of **6c** and **6a,b** (27 °C) the NMR signals of the latter remain sharp. Taking into account that **3b**, which is strongly related to **6c**, is structurally rigid, we exclude the possibility that the dynamics of **6c** are represented by a simple rotation of the $[(d^ippe)Pd^0]$ groups about the coordination axis to the C≡C bond. Instead, we suggest that one of the $[(d^ippe)Pd^0]$ fragments in **6c** migrates to the vinyl bond and *there* the $[(d^ippe)Pd^0]$ fragment rotates about the coordination axis to the (more weakly coordinated) C═C bond. By return to the C≡C bond the pairwise corresponding nuclei of the d^{i}ppe ligand have equilibrated (Scheme 4). The dynamics of the $[(d^ippe)Pd^0]$ fragments in **6c** proceed more easily than in **6a** due to an increased charge at the vinylacetylene ligand. We finally note that at 20 °C a slow solution thermolysis of **6c** starts which does *not* produce alkyne-free **12** (as for **3a,b** ("activated alkyne")), although **2a,b** and **8a,b** ("nonactivated alkynes") do.

(d^{i}ppe)M^0−Butadiyne Complexes (7a−f). We have already communicated that butadiyne is coordinated at Ni(0) to form the mono- and dinuclear complexes (^{i}Pr$_2$P(CH$_2$)$_n$P^{i}Pr$_2$)Ni(η^2-HC≡CC≡CH) (n = 2 (**7a**), 3) and $\{(^i$Pr$_2$P(CH$_2$)$_n$P^{i}Pr$_2$)Ni$\}_2\{\mu$-(1,2-η^2):(3,4-η^2)-HC≡CC≡CH$\}$ (n = 2 (**7b**), 3), which have also been structurally characterized.[20] In addition, for n = 2 (d^{i}ppe) mononuclear derivatives of the heavier homologues (d^{i}ppe)M(η^2-HC≡CC≡CH) (M = Pd (**7c**), Pt (**7f**)) have been synthesized.[6,21] When 1 mol equiv of butadiyne is added to the colorless pentane solution of (d^{i}ppe)Pd(C$_2$H$_4$) at −30 °C, off-white microcrystals of **7c** precipitate in 93% yield. Similarly, the reaction of d^{i}ppe/Pt(cod)$_2$ (cod = 1,5-cyclooctadiene)[22] and butadiyne affords yellow-orange cubes of **7f** (75%) (Scheme 5).

Scheme 5



Complexes **7a,c,f**, as solids and in solution, are stable at ambient temperature for several days. In the EI mass spectra the molecular ions are observed. Cleavage of the butadiyne ligand affords $[(d^ippe)M]^+$ as base ions.[16] The IR and ^{1}H and ^{13}C NMR data of the butadiyne ligands of **7a,c,f** are compiled in Table 3. Concerning the IR spectra, the most characteristic are ν(C−H) and ν(C≡C) of the coordinated C≡C bond, for which the wavenumbers are largest for **7c**, lowest for **7f**, and intermediate for **7a**, consistent with an increase in the back-bonding ability in the series Pd^0 < Ni(0) < Pt(0).[23a,24] With respect to the ^{1}H and ^{13}C NMR data, the downfield complexation shifts of the resonances of the coordinated HC≡C bonds are smallest for **7c**. In a comparison of **7a** and **7f**, the proton resonance of **7f** (δ_H 8.41) is at an exceedingly low field but the ^{13}C resonances are almost coincident.

For **7a,c,f** the ^{31}P NMR spectra display AB type spin systems. It follows from the NMR spectra that all complexes are rigid (relative to the NMR time scale) with respect to both a rotation of the coordinated C≡C bond about the bond axis to the metal and an exchange of coordinated and uncoordinated C≡C bonds.

When **7c** is reacted with (d^{i}ppe)Pd(η^2-C$_6$H$_{10}$), generated in situ from (d^{i}ppe)Pd(η^1-C$_3$H$_5$)$_2$, a brown solution is obtained (0 °C) from which the dinuclear Pd^0−butadiyne complex **7d** crystallizes at −78 °C over the course of several weeks (Scheme 6). Complex **7d** is fairly stable (dec pt >65 °C). The composition is confirmed by the EI mass spectrum (130 °C), which displays the molecular ion (*m*/*e* 786). Loss of the butadiyne ligand affords **12**$^+$, which monomerizes into $[(d^ippe)Pd]^+$. Complex **7d** corresponds to the structurally characterized Ni analogue **7b**, as follows from

(20) Bonrath, W.; Pörschke, K.-R.; Wilke, G.; Angermund, K.; Krüger, C. *Angew. Chem.* **1988**, *100*, 853; *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 833.

(21) Bonrath, W. Dissertation, Universität Bochum, 1988.

(22) The reaction of stoichiometric amounts of Pt(cod)$_2$ and d^{i}ppe in diethyl ether (20 °C) affords (d^{i}ppe)Pt(η^2-cod), which has been spectroscopically characterized.[15a]

(23) Related complexes are as follows. (a) (Ph$_3$P)$_2$Pd{C$_2$(COOMe)$_2$}: Greaves, E. O.; Maitlis, P. M. *J. Organomet. Chem.* **1966**, *6*, 104. Greaves, E. O.; Lock, C. J. L.; Maitlis, P. M. *Can. J. Chem.* **1968**, *46*, 3879 ((Ph$_3$P)$_2$Pd(C$_2$Ph$_2$) is not isolable, see also ref 23c). (b) (Ph$_2$PC$_2$H$_4$PPh$_2$)Pd{C$_2$(COOMe)$_2$}: Moseley, K.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1974**, 169. (c) For (Ph$_3$P)$_2$Pd and (Cy$_3$P)$_2$Pd complexes with hydroxy- and alkoxyalkynes, see: Krause, H.-J. *Z. Anorg. Allg. Chem.* **1982**, *490*, 141. (d) (Cy$_2$PC$_2$H$_4$PCy$_2$)Pd{C$_2$(COOMe)$_2$}: Schick, K.-P. Dissertation, Universität Bochum, 1982. Jolly, P. W. *Angew. Chem.* **1985**, *97*, 279; *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 283. Pan, Y.; Mague, J. T.; Fink, M. J. *Organometallics* **1992**, *11*, 3495. See also ref 27. For (Cy$_2$PC$_2$H$_4$PCy$_2$)Pd(C$_2$Ph$_2$) and $\{$(Cy$_2$PC$_2$H$_4$PCy$_2$)Pd$\}_2(\mu$-C$_2$Ph$_2$), see ref 27. (e) Although (^{i}Pr$_3$P)$_2$Pd(C$_2$H$_2$)[3,12] has been isolated, (^{i}Pr$_3$P)$_2$Pd(C$_2$Ph$_2$) appears to be unstable. Cestaric, G. Diplomarbeit, Universität Düsseldorf, 1996.

(24) (a) Farrar, D. H.; Payne, N. C. *J. Organomet. Chem.* **1981**, *220*, 251. (b) Rosenthal, U.; Oehme, G.; Görls, H.; Burlakov, V. V.; Polyakov, A. V.; Yanovsky, A. I.; Struchkov, Y. T. *J. Organomet. Chem.* **1990**, *389*, 251.

Table 3. IR (Raman) and ^{1}H and ^{13}C NMR Data (THF-d_8, −30 °C) of Butadiyne and the Butadiyne Ligand of Mononuclear (d^{i}ppe)M(η^2-HC≡CC≡CH) (M = Ni (7a), Pd (7c), Pt (7f)) and Dinuclear {(d^{i}ppe)M}$_2$(μ-η^2:η^2-HC≡CC≡CH) (M = Ni (7b), Pd (7d,e))[a]

	ν (cm^{-1})				δ_H		δ_C					
							≡CH$_{coord}$		≡C−$_{coord}$		≡CH$_{free}$		≡C−$_{free}$	
compd (M)	C−H$_{free}$	C−H$_{coord}$	C≡C$_{free}$	C≡C$_{coord}$	≡CH$_{coord}$	≡CH$_{free}$								
C_4H_2			2172 (Ra) sym			2.06					65.3	^{1}J(CH) 259	67.5	
	3341/24 asym[b]		2027/11 asym[b]											
7a (Ni)	3307	3057	2068	1669	7.44	4.43	129.5	^{1}J(CH) 200	122.1	^{2}J(CH) 11	90.4	^{1}J(CH) 248	81.4	^{2}J(CH) 50
7c (Pd)	3314	3075[c]	2066	1690	7.19	4.10	112.8	^{1}J(CH) 210	106.9	^{2}J(CH) 10	86.6	^{1}J(CH) 249	80.7	^{2}J(CH) 52
7f (Pt)	3311	3049	2062	1621	8.41	4.06	130.2	^{1}J(PtC) 327	120.4	^{1}J(PtC) 303	87.6	^{3}J(PtC) 20	82.7	^{2}J(PtC) 33
								^{1}J(CH) 200		^{2}J(CH) 10		^{1}J(CH) 249		^{2}J(CH) 50
7b (Ni)		3085		1760/1601	6.85		116.3	^{1}J(CH) 202	132.1					
7d (Pd)		3124		1820/1638	6.55		99.7		115.7					
7e (Pd)	*d*	*d*	*d*	*d*	5.37	2.93	69.0	^{1}J(CH) 191	61.5	^{2}J(CH) 12	70.8	^{1}J(CH) 243	92.0	^{2}J(CH) 50

[a] Coupling constants in hertz. [b] Gaseous butadiyne; P and R branches. [c] Very weak. [d] Not recorded.

Scheme 6

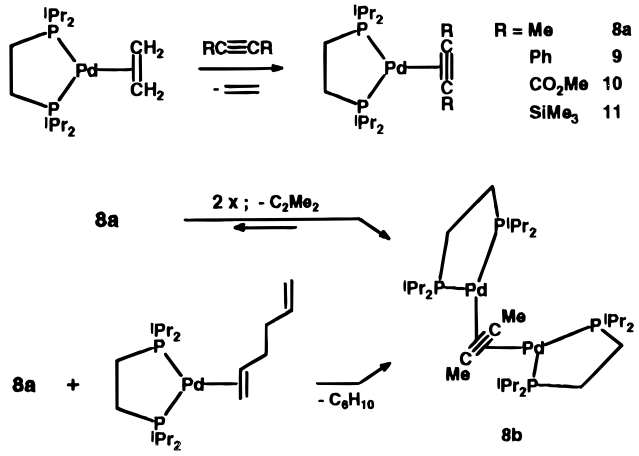
concurring butadiyne ligand IR and NMR data (Table 3). Again, the coordination shifts of the butadiyne ligand IR bands and NMR resonances are smaller for **7d** than for **7b**, in agreement with a lower back-bonding strength of Pd^0 as compared to Ni(0). The d^{i}ppe NMR signals of **7d** indicate C_{2v} or C_{2h} symmetry in solution. Thus, the two [(d^{i}ppe)Pd] moieties in **7d** are coordinated at *different* C≡C bonds of a bridging butadiyne ligand.

When a THF-d_8 solution of **7d** is kept at −80 °C, a slow isomerization takes place to afford **7e**. The isomerization is complete after about 1 week. According to the ^{1}H and ^{13}C NMR spectra (Table 3) the [(d^{i}ppe)Pd] moieties in **7e** are coordinated to the *same* C≡C bond of a bridging butadiyne ligand (similar to the case for **2b**, **3b**, and **6c**). Thereby, a rather rigid structure results, and the symmetry of the complex is lowered to C_s. When the solution of **7e** is warmed to 0 °C, the isomerization is only partially reversed. It has not been attempted to isolate **7e**. Apparently, isomers **7d** and **7e** are in slow equilibrium and subtle effects determine which one is preferred. While **7e** is thermodynamically favored in solution, crystallization affords **7d**.

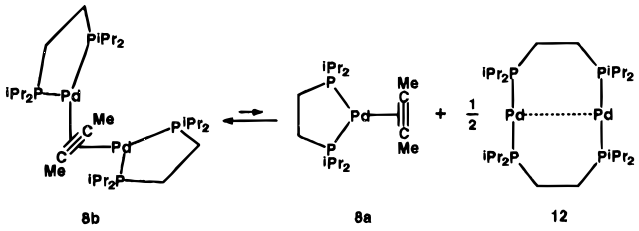
(d^{i}ppe)Pd^0 Complexes with MeC≡CMe, PhC≡C-Ph, MeO$_2$CC≡CCO$_2$Me, and Me$_3$SiC≡CSiMe$_3$ (8−11). For reasons of comparison we have also prepared some (d^{i}ppe)Pd^0 complexes with internal alkynes. The substituents of these alkynes are of the same kind as in the case of the 1-alkyne complexes **2**−**5**. When to a solution of (d^{i}ppe)Pd(C_2H_4) in pentane or diethyl ether 2-butyne (0 °C), tolane, acetylenedicarboxylic acid dimethyl ester, and bis(trimethylsilyl)acetylene (all 20 °C) are added, colorless off-white crystals of the mononuclear complexes **8a** and **9**−**11** are obtained in 80−90% yield (Scheme 7).[23] Solutions of **9**−**11** are stable at 20 °C for at least several days. Complex **8a** partially eliminates 2-butyne in solution to produce small amounts of dinuclear **8b**. The latter has been prepared in a pure state by treating **8a** with (d^{i}ppe)Pd(η^2-C_6H_{10}), obtained in situ from (d^{i}ppe)Pd(η^1-C_3H_5)$_2$, to afford yellow crystals of **8b** in 85% yield.[25] When a solution of **8b** in THF-d_8 is kept at 20 °C for a few hours, the ^{31}P NMR spectrum shows, besides the singlet of **8b** (δ_P 56.4, 70%), additional singlets of equal intensity (each 15%) for mononuclear **8a** (δ_P 67.1) and dinuclear alkyne-free **12** (δ_P 33.7) due to an equilibrium between these complexes (Scheme 8). No byproducts are detected. Complex **12**

(25) Without question dinuclear derivatives of **9**−**11** can also be prepared by applying a procedure similar to that for **8b**, although this has not been attempted by us.

Scheme 7



Scheme 8



is exceedingly soluble in ordinary solvents and has not been isolated so far.[26] It is assumed that **12** is analogous to the structurally characterized $Pd_2\{\mu\text{-}(c\text{-}C_6H_{11})_2PC_2H_4P(c\text{-}C_6H_{11})_2\}_2$.[27]

Properties of 8−11. The melting points of the mono- and dinuclear 2-butyne complexes **8a,b** (about 80 °C) and of the $Me_3SiC{\equiv}CSiMe_3$ complex **11** (50 °C) are rather low, whereas those of the other derivatives are higher (**9**, 166 °C; **10**, 101 °C). Solutions of **9**−**11** and added alkyne (C_2Ph_2, $C_2(COOMe)_2$, or $C_2(SiMe_3)_2$) show no reaction at 20 °C over several days,[28] in contrast to the corresponding 1-alkyne complexes. In the EI mass spectra of the mononuclear complexes (**8a**, **9**−**11**) the molecular ions are observed, whereas for dinuclear **8b** the largest detected ion is alkyne-free $[(d^i\text{ppe})_2Pd_2]^+$ (**12**$^+$, 23%). In the IR spectra (Table 1) the C≡C stretching frequencies of the disubstituted alkyne ligands occur at 1840 ± 30 cm^{-1} (**11**, 1771 cm^{-1}) and thus, as expected, are at higher wavenumbers than for the 1-alkyne complexes. The complexation shift $\Delta\nu$(C≡C) of the disubstituted alkyne ligands, however, is of magnitude similar to that for the corresponding 1-alkyne complexes.

The ^{1}H and ^{31}P NMR spectra of **9**−**11** (Table 2) are not very informative and serve only to confirm the composition and purity of the complexes. The ^{13}C resonances of the (quaternary) C≡C atoms represent for **9** an ABX multiplet and for **10** a doublet ($^2J(PC)_{trans}$ = 74 Hz; $^2J(PC)_{cis}$ is very small). Thus, different couplings to *trans* and *cis* ^{31}P nuclei are observed in agreement with a static C≡C bond coordination in these complexes.

Concerning the 2-butyne complexes **8a,b**, the ^{13}C multiplet structure of the 2-butyne C≡C atoms has not been sufficiently resolved to allow an unequivocal assignment to a certain spin system (ABX, A_2X, A_2B_2X, or A_4X). However, the CH_3 ^{1}H resonance of the 2-butyne ligand in mononuclear **8a** (δ_H 2.51) also represents an ABX multiplet, whereas the corresponding CH_3 signal of dinuclear **8b** (δ_H 2.86) is a sharp A_4X quintet at 27 °C (unresolved at −30 °C). It is concluded from these spectra that at ambient temperature and relative to the NMR time scale the rotation of the $(d^i\text{ppe})Pd^0$ moieties about the bond axis to the 2-butyne ligand is slow for **8a** (similar as for the propyne complex **2a**) but rapid for **8b** (in contrast to **2b**). The anticipated bond rotation in **8b** is presumably due to the increased charge at the bridging C≡C bond, resulting from the inductive effect of two Me substituents and back-bonding from two Pd^0 centers.

Discussion

We have described a series of novel mono- and dinuclear $(d^i\text{ppe})Pd^0$−1-alkyne complexes (**2**−**7**) and also some derivatives with internal alkynes (**8**−**11**). Although the former are in general thermally somewhat less stable than the latter, the Pd^0−1-alkyne complexes should not be regarded as particularly unstable, in contrast to prior perception. The following features of the complexes are worth emphasizing:

(a) The relatively small and "fixed" bite of the *d^{i}ppe ligand* at Pd^0 (87.2°), as compared to monodentate phosphanes and to bidentate ligands $R'_2P(CH_2)_nPR'_2$ (n > 2) forming larger chelate rings, contributes to the stabilization of the complexes because of an increased back-donation from Pd^0 to the alkyne ligand. Thus, no alkyne ligand dissociation has been observed on the NMR time scale, in contrast to, e.g., extensive alkyne ligand dissociation of $(^iPr_3P)_2Pd(C_2Ph_2)$.[23e]

(b) As one might expect, *alkyne coordination* to the $[(d^i\text{ppe})Pd^0]$ fragment is generally weaker for alkynes with electron-donating substituents and stronger for those with electron-withdrawing substituents. Thus, in solution the mononuclear complexes **2a** and **8a** slowly eliminate propyne or 2-butyne to form the dinuclear complexes **2b** and **8b** as primary products. Similarly, while monophenyl-substituted **3a** slowly eliminates PhC_2H to form **3b**, the tolane derivative **9** is stable. In contrast, for COOMe- and $SiMe_3$-substituted alkynes the mononuclear complexes (**4**, **10** and **5**, **11**) are stable.

For the mononuclear Pd^0−alkyne complexes the IR and ^{13}C NMR complexation shifts $\Delta\nu$(C≡C) and $\Delta\delta$(C≡C) respectively display an approximately linear correlation with the inductive effect substituent constant σ_I[29a] of R.[29b] The data confirm similar correlations established before for related alkyne complexes.[30]

(26) In solution, $Pd_2(\mu\text{-}d^i\text{ppe})_2$ (**12**; $C_{28}H_{64}P_4Pd_2$, M_r = 737.6) has been encountered before by various groups. (a) Hopp, G.; Jolly, P. W.; Krause, J.; Pörschke, K.-R. Unpublished results. (b) When an ethereal solution of $(d^i\text{ppe})Pd\{\eta^2\text{-}CH_2{=}C(Me)C_2H_4C(Me){=}CH_2\}$, obtained from $(d^i\text{ppe})Pd(\eta^1\text{-}2\text{-}MeC_3H_4)_2$[3] at 20 °C, is evaporated to dryness, the color changes to deep red. In the ^{1}H and ^{31}P NMR spectra (THF-d_8) of the residue the signals of **12** are observed: ^{1}H NMR (200 MHz, 27 °C) δ 1.80 (8 H, PCH), 1.75 (8 H, PCH_2), 1.26, 1.22 (each 24 H, diastereotopic Me); ^{31}P NMR δ 33.7; EI-MS (70 eV, 160 °C) m/e 736 (M^+).[15a] (c) Fryzuk, M. D.; Clentsmith, G. K. B.; Rettig, S. J.; Hägele, G. *Organometallics* **1996**, *15*, 2083.

(27) Pan, Y.; Mague, J. T.; Fink, M. J. *J. Am. Chem. Soc.* **1993**, *115*, 3842. Landtiser, R.; Pan, Y.; Fink, M. J. *Phosphorus, Sulfur Silicon Relat. Elem.* **1994**, *93*−*94*, 393.

(28) $C_6(COOMe)_6$, the cyclotrimer of $C_2(COOMe)_2$, can easily be excluded because of the absence of the corresponding ^{1}H NMR signal (δ_H 3.88). Diercks, R.; tom Dieck, H. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1984**, *39*, 180.

(29) (a) Charton, M. *Prog. Phys. Org. Chem.* **1981**, *13*, 119. (b) For unsymmetrical alkynes, σ_I and $\Delta\delta$(C≡C) are defined as $\sigma_I = \{\sigma_I(R^1) + \sigma_I(R^2)\}/2$ and $\Delta\delta(C{\equiv}C) = \{\Delta\delta(C^1) + \Delta\delta(C^2)\}/2$, respectively.

(30) (a) Herberich, G. E.; Okuda, J. *Chem. Ber.* **1984**, *117*, 3112. (b) Rosenthal, U.; Schulz, W. *J. Organomet. Chem.* **1987**, *321*, 103. Rosenthal, U.; Oehme, G.; Burlakov, V. V.; Petrovskii, P. V.; Shur, V. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *391*, 119.

(c) As determined by NMR, the mononuclear (d^ippe)-Pd^0−alkyne complexes of ethyne, 1-alkynes, and internal alkynes are rigid (27 °C) with respect to a possible *alkyne ligand rotation* about the bond axis to Pd^0. While this also holds for dinuclear **1b** (ethyne) and largely for **2b** (propyne), a corresponding rotation indeed takes place in the case of **8b**, where the 2-butyne ligand is relatively electron-rich.

(d) With respect to possible *secondary reactions*, initiated for example by a C−H activation step of the 1-alkyne, the pure (d^ippe)Pd^0−1-alkyne complexes are surprisingly stable. Such a reaction has to be taken into account only when an excess of the 1-alkyne is present, thereby facilitating an anticipated C−H addition of a further alkyne molecule to the initially formed 16e complex by an associative mechanism. This secondary reaction is especially severe for the $MeO_2CC{\equiv}CH$ complex **4**, which may explain why former attempts to synthesize such complexes had failed. Secondary reactions are retarded by carrying out the synthesis of the complexes at low temperature.

In conclusion, due to the electronic and steric properties (strong chelate effect) of the d^ippe ligand the [(d^ippe)Pd^0] fragment withstands a lowering of the phosphane ligation from L_2Pd^0 to L−Pd^0 or phosphane-free Pd^0, which are considered to be catalytically more active species,[10,23b] and as a result L_2Pd^0−1-alkyne complexes are easily isolable.[31]

Experimental Section

To exclude oxygen and moisture, all operations were conducted under an atmosphere of argon by standard Schlenk techniques. Pd(η^3-C_3H_5)$_2$,[32] Pd(η^3-2-MeC_3H_4)$_2$,[32] (d^ippe)Pd(η^1-C_3H_5)$_2$,[2] (d^ippe)Pd(η^1-2-MeC_3H_4)$_2$,[3] (d^ippe)Pd(C_2H_4),[2] and Pt(cod)$_2$[33] were prepared by published procedures. Microanalyses were performed by the Mikroanalytisches Labor Kolbe, Mülheim, Germany. ^{1}H NMR spectra (δ relative to internal TMS) were measured at 200, 300, and 400 MHz, ^{13}C NMR spectra (δ relative to internal TMS) at 50.3, 75.5, and 100.6 MHz, and ^{31}P NMR spectra (δ relative to external 85% aqueous H_3PO_4) at 81, 121.5, and 162 MHz on Bruker AM-200, WM-300, and WH-400 instruments. For all NMR spectra solutions of the compounds in THF-d_8 were used. EI mass spectra were recorded at 70 eV on a Finnigan MAT 8200, IR spectra on Nicolet FT 7199 and Magna-IR 750 spectrometers, and Raman spectra on a Coderg LRT 800 spectrometer (excitation by argon ion laser at 4880 Å).

(d^ippe)Pd(MeC≡CH) (2a). To the colorless pentane solution (10 mL) of (d^ippe)Pd(C_2H_4) (1.984 g, 5.0 mmol) is added propyne (1 mL, 17.6 mmol) at −30 °C. The mixture is warmed to 0 °C, whereupon the color changes to orange. After filtration (D4 glass frit) to remove insoluble impurities, orange microcrystals separate at −78 °C. The mother liquor is cannulated away from the solid. The latter is subsequently washed twice with cold pentane and dried under vacuum at −30 °C: yield 1.62 g (79%); mp 38 °C dec. Anal. Calcd for $C_{17}H_{36}P_2Pd$ (408.8): C, 49.94; H, 8.88; P, 15.15; Pd, 26.03. Found: C, 49.66; H, 9.15; P, 15.10; Pd, 25.91. EI-MS (50 °C): *m*/*e* (%) 408 (M^+, 10), 368 ([(d^ippe)Pd]$^+$, 100), 40 ([MeC≡CH]$^+$, 78). IR (KBr): see Table 1. ^{1}H NMR (200 MHz, −30 °C): δ 6.21 (m, 1 H, ≡CH), 2.64 (m, 3 H, ≡CMe), propyne; 2.0 (4 H, PCH and P′CH), 1.6 (4 H, PCH_2 and P′CH_2), 1.1 (four unresolved signals 24 H, Me), d^ippe. ^{13}C NMR (100.6 MHz, −80 °C): δ 116.6 [1 C, $^2J(PC)_{trans}$ = 52.5 Hz, $^2J(PC)_{cis}$ = 24.3 Hz, ^2J(CH) = 9 Hz, ≡CMe], 96.4 [1 C, ^1J(CH) = 212 Hz, $^2J(PC)_{trans}$ = 56.0 Hz, $^2J(PC)_{cis}$ = 2.9 Hz, ≡CH], 17.6 [1 C, ^3J(PC) = 19.1 Hz, ^3J(PC) = 12.4 Hz, Me], propyne; 26.0, 25.9 [each 1 C, ^1J(PC) = 4.8 Hz, PCH and P′CH], 22.7, 22.3 [each 1 C, ^1J(PC) = 18 Hz, PCH_2 and P′CH_2], 20.3 [4 C, ^2J(PC) = 10.5 Hz, set of diastereotopic Me], 18.9 [4 C, ^2J(PC) = 15.3 Hz, set of diastereotopic Me], d^ippe. ^{31}P NMR (81 MHz, −30 °C): see Table 2. ^{31}P NMR (81 MHz, 27 °C): δ 68.2 (coalesced signal).

{(d^ippe)Pd}$_2$(μ-MeC≡CH) (2b). An ethereal solution (5 mL) of **2a** (409 mg, 1.0 mmol) is combined at −78 °C with a cream-colored suspension of (d^ippe)Pd(η^1-C_3H_5)$_2$ (451 mg, 1.0 mmol) in diethyl ether (10 mL). When the mixture is warmed to 0 °C, a yellow solution is obtained from which off-white crystals separate at −30/−78 °C. The product is isolated as described above and dried under vacuum at 0 °C: yield 620 mg (80%); mp 70 °C dec. Anal. Calcd for $C_{31}H_{68}P_4Pd_2$ (777.6): C, 47.88; H, 8.81; P, 15.93; Pd, 27.37. Found: C, 47.83; H, 8.82; P, 15.76; Pd, 27.53. EI-MS (120 °C): *m*/*e* (%) 736 (**12**$^+$, 3), 368 ([(d^ippe)Pd]$^+$, 100), 40 ([MeC≡CH]$^+$, 50). IR (KBr): see Table 1. ^{1}H NMR (300 MHz, −30 °C): δ 5.44 [tt, 1 H, $^3J(PH)_{trans}$ = 18 Hz, $^3J(PH)_{cis}$ = 6 Hz, ≡CH], 2.92 [t, 3 H, ^4J(PH) = 8 Hz, ≡CMe], propyne; 2.0−1.7 (four unresolved signals, 8 H, PCH), 1.5−1.3 (four unresolved signals, 8 H, PCH_2), 1.1−0.8 (eight unresolved signals, 48 H, Me), d^ippe. ^{13}C NMR (75.5 MHz, −30 °C): δ 85.4 [tt, 1 C, $^2J(PC)_{trans}$ = 47 Hz, $^2J(PC)_{cis}$ = 6 Hz, ≡CMe], 67.7 [tt, 1 C, ^1J(CH) = 196 Hz, $^2J(PC)_{trans}$ = 46 Hz, $^2J(PC)_{cis}$ = 7 Hz, ≡CH], ∼26 (obscured CH_3), propyne; 25.9 (8 C, four unresolved signals PCH), 22.7 (4 C, PCH_2 and P′CH_2), 21.1, 20.8, 20.3, 20.0, 19.6 (each 2 C), 18.9 (4 C), 18.7 (2 C, Me), d^ippe. ^{31}P NMR (121.5 MHz, −30 °C): see Table 2.

(d^ippe)Pd(PhC≡CH) (3a). To a colorless solution of (d^ippe)Pd(C_2H_4) (794 mg, 2.0 mmol) in diethyl ether (10 mL) is added PhC≡CH (0.5 mL, 4.5 mmol) at 0 °C. When the solution is cooled to −30/−78 °C, colorless crystals are obtained, which are isolated as described above and dried under vacuum at 20 °C: yield 735 mg (78%); mp 81 °C. Anal. Calcd for $C_{22}H_{38}P_2Pd$ (470.9): C, 56.11; H, 8.13; P, 13.15; Pd, 22.60. Found: C, 56.21; H, 7.99; P, 13.21; Pd, 22.60. EI-MS (50 °C): *m*/*e* (%) 470 (M^+, 6), 368 ([(d^ippe)Pd]$^+$, 100), 102 ([PhC≡CH]$^+$, 94). IR (KBr): see Table 1. ^{1}H NMR (200 MHz, 27 °C): δ 7.51 (C_βH), 7.17 (C_γH), 7.01 (C_δH, C_6H_5), 7.36 [dd, 1 H, $^3J(PH)_{trans}$ = 30.8 Hz, $^3J(PH)_{cis}$ = 16.5 Hz, ≡CH], alkyne; 2.1 (4 H, PCH and P′CH), 1.7 (4 H, PCH_2 and P′CH_2), 1.1 (four unresolved signals, 24 H, Me), d^ippe. ^{13}C NMR (50.3 MHz, 27 °C): δ 133.0 (1 C, C_α), 131.9 (2 C, C_β), 128.5 (2 C, C_γ), 126.0 (1 C, C_δ, C_6H_5), 129.4 (1 C, ≡C− quaternary), 107.7 [1 C, $^2J(PC)_{trans}$ = 64 Hz, $^2J(PC)_{cis}$ = 3 Hz, ≡CH], alkyne; 27.1 [2 C, ^1J(PC) = 11.3 Hz, ^3J(P′C) = 4.4 Hz, PCH], 26.4 [2 C, ^1J(P′C) = 10.5 Hz, ^3J(PC) = 3.5 Hz, P′CH], 23.8 [1 C, ^1J(PC) = 20.1 Hz, ^2J(P′C) = 17.4 Hz, PCH_2], 23.0 [1 C, ^1J(P′C) ≈ ^2J(PC) ≈ 17 Hz, P′CH_2], 20.8, 20.8, 19.7, 19.4 (each 2 C, Me), d^ippe. ^{31}P NMR (81 MHz, 27 °C): see Table 2.

Crystal Structure Determination of 3a. A crystal (yellow plates) of dimensions 0.32 × 0.53 × 0.53 mm was used for X-ray crystallography. Preliminary examination and data collection were performed at 20 °C with Mo Kα radiation (λ = 0.710 69 Å) on an Enraf-Nonius CAD4 diffractometer equipped with a graphite incident beam monochromator. Crystal data: $C_{22}H_{38}P_2Pd$, M_r = 470.86, monoclinic, space group $P2_1/n$ (No. 14), a = 12.0451(14) Å, b = 15.1265(14) Å, c = 14.382(3) Å, β = 110.467(12)°, V = 2455.0(6) Å^3, Z = 4, D_{calcd} = 1.274 g cm^{-3}, absorption coefficient 0.889 mm^{-1}, F(000) = 984, no absorption correction. A total of 5807 measured reflections, 5593 unique, were obtained using an ω−2θ scan technique with a scan rate of 1−5° min^{-1} (in ω). The structure was solved by SHELXS-86[34] and refined by SHELXL-93[35] (on F^2) to a final R1 = 0.0375, wR2 = 0.0891 (observed reflections).

(31) Concerning Pd^0 ligated by *monodentate* phosphanes, besides the isolated (Me_3P)$_2$Pd(HC≡CH)[12] and (^{i}Pr$_3$P)$_2$Pd(HC≡CH)[12] we have characterized (Me_3P)$_2$Pd(Me_3SiC≡CH) in solution (NMR).[3]

(32) See ref 2 and literature cited therein.

(33) (a) Müller, J.; Göser, P. *Angew. Chem.* **1967**, *79*, 380; *Angew. Chem., Int. Ed. Engl.* **1967**, *6*, 364. (b) Green, M.; Howard, J. A. K.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 271. (c) Herberich, G. E.; Hessner, B. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1979**, *34*, 638. (d) Crascall, L. E.; Spencer, J. L. *Inorg. Synth.* **1990**, *28*, 126.

{(d^{i}ppe)Pd}$_2$(μ-PhC≡CH) (3b). An ethereal solution (5 mL) of **3a** (471 mg, 1.0 mmol) is combined at −78 °C with a suspension of (d^{i}ppe)Pd(η^1-C$_3$H$_5$)$_2$ (451 mg, 1.0 mmol) in diethyl ether (10 mL), and the mixture is warmed to 20 °C (15 min). The resulting orange solution is filtered to remove some insoluble impurities. Cooling the solution to −78 °C affords orange intergrown needles, which are isolated as described above and dried under vacuum at 20 °C: yield 665 mg (79%); mp 110 °C dec. Anal. Calcd for $C_{36}H_{70}P_4Pd_2$ (839.7): C, 51.49; H, 8.40; P, 14.75; Pd, 25.35. Found: C, 51.42; H, 8.34; P, 14.73; Pd, 25.47. EI-MS (120 °C): *m/e* (%) 838 (M$^+$, 2), 736 (**12**$^+$, 3), 368 ([(d^{i}ppe)Pd]$^+$, 44), 102 ([PhC≡CH]$^+$, 41). IR (KBr): see Table 1. ^{1}H NMR (300 MHz, 27 °C): δ 7.48 (C$_\beta$H), 6.89 (C$_\gamma$H), 6.61 (C$_\delta$H, C$_6$H$_5$), 5.78 [tt, 1 H, ^3J(PH)$_{trans}$ = 19.5 Hz, ^3J(PH)$_{cis}$ = 5.7 Hz, ≡CH], alkyne; 2.1−1.8 (4 unresolved signals, 8 H, PCH), 1.6−1.4 (4 unresolved signals, 8 H, PCH$_2$), 1.22 (12 H), 1.12 (12 H), 1.02 (12 H), 0.85 (6 H), 0.74 (6 H), CH$_3$, d^{i}ppe. ^{13}C NMR (75.5 MHz, 27 °C): δ 148.7 [tt, ^3J(PC)$_{trans}$ = 8 Hz, ^3J(PC)$_{cis}$ = 3 Hz, C$_\alpha$H], 130.7 (C$_\beta$H), 127.1 (C$_\gamma$H), 121.1 (C$_\delta$H, C$_6$H$_5$), 92.2 [tt, ^2J(PC)$_{trans}$ = 50.4 Hz, ^2J(PC)$_{cis}$ = 5.6 Hz, −C≡], 66.6 [m, ^1J(CH) = 197.5 Hz, ≡CH], alkyne; 26.6, 26.3, 26.1, 25.7 (each 2 C, PCH), 23.2, 22.3 (each 2 C, PCH$_2$), 21.3, 21.1, 20.2, 19.9, 19.8, 19.6, 18.6, 18.1 (each 2 C, CH$_3$), d^{i}ppe. ^{31}P NMR (121.5 MHz, 27 °C): see Table 2.

(d^{i}ppe)Pd(MeO$_2$CC≡CH) (4). To the colorless solution of (d^{i}ppe)Pd(C$_2$H$_4$) (794 mg, 2.0 mmol) in diethyl ether (5 mL) is added at −30 °C an ethereal solution (5 mL) of MeO$_2$CC≡CH (0.5 mL, 5.6 mmol). When the solution is concentrated under vacuum to a volume of 4 mL, a tan microcrystalline precipitate is obtained (−30 °C), which is isolated as described above and dried under vacuum at 0 °C: yield 790 mg (87%); mp 56 °C. Anal. Calcd for $C_{18}H_{36}O_2P_2Pd$ (452.9): C, 47.74; H, 8.01; O, 7.07; P, 13.68; Pd, 23.50. Found: C, 47.90; H, 7.95; P, 13.62; Pd, 23.38. EI-MS (40 °C): *m/e* (%) 452 (M$^+$, 2), 368 ([(d^{i}ppe)-Pd]$^+$, 100). IR (KBr): 1667, 1175 cm^{-1} (CO$_2$Me); for alkyne ligand, see Table 1. ^{1}H NMR (200 MHz, 27 °C): δ 7.36 [dd, 1 H, ^3J(PH)$_{trans}$ = 28.7 Hz, ^3J(PH)$_{cis}$ = 19.1 Hz, HC≡], 3.61 (s, 3 H, Me), alkyne; 2.0 (4 H, PCH and P′CH), 1.7 (4 H, PCH$_2$ and P′CH$_2$), 1.1 (four unresolved signals, 24 H, Me), d^{i}ppe. ^{13}C NMR (75.5 MHz, 27 °C): δ 169.9 [dd, 1 C, ^3J(PC)$_{trans}$ = 18 Hz, ^3J(PC)$_{cis}$ = 13 Hz, *C*OOMe], 117.5 [d, 1 C, ^2J(PC)$_{trans}$ = 62.1 Hz, ^2J(PC)$_{cis}$ = 3.1 Hz, −C≡], 112.2 [d, 1 C, ^2J(PC)$_{trans}$ = 71.2 Hz, ^2J(PC)$_{cis}$ = 2.0 Hz, ^1J(CH) = 210 Hz, ≡CH], 50.9 (1 C, OMe), alkyne; 25.9 (2 C, PCH), 25.7 (2 C, P′CH), 23.0 (1 C, PCH$_2$), 22.7 (1 C, P′CH$_2$), 20.3, 19.9, 19.3, 19.2 (each 2 C, Me), d^{i}ppe. ^{31}P NMR (81 MHz, 27 °C): see Table 2.

(d^{i}ppe)Pd(Me$_3$SiC≡CH) (5). To the colorless solution of (d^{i}ppe)Pd(C$_2$H$_4$) (782 mg, 2.0 mmol) in pentane (10 mL) is added at −30 °C Me$_3$SiC≡CH (0.5 mL, 3.5 mmol). At −78 °C off-white crystals slowly separate (1 day), which are isolated as described above and dried under vacuum at 0 °C: yield 847 mg (92%); mp 30 °C. Anal. Calcd for $C_{19}H_{42}P_2PdSi$ (467.0): C, 48.87; H, 9.07; P, 13.27; Pd, 22.79; Si, 6.01. Found: C, 48.78; H, 8.99; P, 13.25; Pd, 22.65; Si, 6.11. EI-MS (20 °C): *m/e* (%) 466 (M$^+$, 6), 368 ([(d^{i}ppe)Pd]$^+$, 100), 98 ([Me$_3$-SiC≡CH]$^+$, 5), 83 ([Me$_2$SiC≡CH]$^+$, 40). IR (KBr): 1238, 855/34 cm^{-1} (SiMe$_3$); for alkyne ligand, see Table 1. ^{1}H NMR (200 MHz, 27 °C): δ 7.26 [dd, 1 H, ^3J(PH)$_{trans}$ = 32.6 Hz, ^3J(PH)$_{cis}$ = 15.1 Hz, ≡CH], 0.19 (s, 9 H, SiMe$_3$), alkyne; 2.0 (4 H, PCH and P′CH), 1.65 (4 H, PCH$_2$ and P′CH$_2$), 1.16, 1.09, 1.04, 0.98 (each, 6 H, Me), d^{i}ppe. ^{13}C NMR (50.3 MHz, 27 °C): δ 121.3 [1 C, ^2J(PC)$_{trans}$ = 46.2 Hz, ^2J(PC)$_{cis}$ = 9.6 Hz, ≡CH], 116.3 [1 C, ^2J(PC)$_{trans}$ = 36.6 Hz, ^2J(PC)$_{cis}$ = 8.7 Hz, −C≡], 2.0 (3 C, SiMe$_3$), alkyne; 26.7 (4 C, PCH and P′CH), 24.2 [1 C, ^1J(PC) = 20.9 Hz, ^2J(P′C) = 17.4 Hz, PCH$_2$], 23.1 [1 C, ^1J(P′C) = 17.4 Hz, ^2J(PC) = 15.7 Hz, P′CH$_2$], 21.1, 20.6, 19.7, 19.4 (each 2 C, Me), d^{i}ppe. ^{31}P NMR (81 MHz, 27 °C): see Table 2.

(d^{i}ppe)Pd(H$_2$C=CHC≡CH) (6a,b). To the colorless solution of (d^{i}ppe)Pd(C$_2$H$_4$) (794 mg, 2.0 mmol) in pentane (20 mL) is added at −30 °C vinylacetylene (1 mL, 13.6 mmol). When the solution is cooled to −78 °C, colorless crystals form, which are separated as described above and dried under vacuum at −30 °C: yield 810 mg (96%); mp 76 °C dec. Anal. Calcd for $C_{18}H_{36}P_2Pd$ (420.9): C, 51.37; H, 8.62; P, 14.72; Pd, 25.29. Found: C, 51.33; H, 8.64; P, 14.78; Pd, 25.28. EI-MS (50 °C): *m/e* (%) 420 (M$^+$, 6), 368 ([(d^{i}ppe)Pd]$^+$, 100), 52 ([H$_2$C=CHC≡CH]$^+$, 96).

6a: IR (KBr) 3087 (H−C≡ coord), 3009 (H−C= free), 1717 (C≡C coord), 1582 cm^{-1} (C=C free); ^{1}H NMR (400 MHz, −80 °C) δ 7.13 [dd, 1 H, ^3J(PH)$_{trans}$ = 30.5 Hz, ^3J(PH)$_{cis}$ = 17.0 Hz, ≡CH], 6.97 (m, 1 H, =CH−), 5.40 [m, 1 H, ^2J(HH) = 2.5 Hz, ^3J(HH) = 16.2 Hz, =CHH$_Z$], 5.25 [dd, 1 H, ^2J(HH) = 2.5 Hz, ^3J(HH) = 9.4 Hz, =CH$_E$H], alkyne, 2.19, 2.06 (each m, 2 H, PCH and P′CH), 1.7 (4 H, PCH$_2$ and P′CH$_2$), 1.06 (four unresolved signals, 24 H, Me), d^{i}ppe; ^{13}C NMR (100.6 MHz, −80 °C) δ 128.1 [dd, 1 C, ^3J(PC)$_{trans}$ = 17.2 Hz, ^3J(PC)$_{cis}$ = 10.9 Hz, −CH=], 123.5 [dd, 1 C, ^2J(PC)$_{trans}$ = 63.0 Hz, ^2J(PC)$_{cis}$ = 3.8 Hz, ≡C−], 120.7 (1 C, =CH$_2$), 109.8 [dd, 1 C, ^2J(PC)$_{trans}$ = 65.8 Hz, ^2J(PC)$_{cis}$ = 3.8 Hz, ≡CH], alkyne; 27.1, 26.0 (each 2 C, PCH and P′CH), 23.1, 21.8 (each 1 C, PCH$_2$ and P′CH$_2$), 20.7, 20.2, 18.7, 18.7 (each 2 C, Me), d^{i}ppe; ^{31}P NMR (162 MHz, −80 °C), see Table 2.

6b: IR (KBr) 3317 (H−C≡ free), 2069 cm^{-1} (C≡C free); ^{1}H NMR (200 MHz, 27 °C) δ 3.12 (m, 1 H, =CH−), 2.63 (m, 1 H, ≡CH), 2.49, 2.36 (each m, 1 H, =CHH$_Z$ and =CH$_E$H), alkyne, d^{i}ppe signals as for **6a**; ^{31}P NMR (81 MHz, 27 °C) δ 66.8, 60.4 [^2J(PP) = 43 Hz].

{(d^{i}ppe)Pd}$_2$(μ-H$_2$C=CHC≡CH) (6c). An ethereal solution (15 mL) of **6a,b** (421 mg, 1.0 mmol) is added at −78 °C to (d^{i}ppe)Pd(η^1-C$_3$H$_5$)$_2$ (451 mg, 1.0 mmol), and the mixture is warmed to 0 °C (5 min). The resulting orange solution is filtered to remove insoluble impurities. At −78 °C orange crystals are obtained, which are isolated as described above and dried under vacuum at −30 °C: yield 625 mg (79%); dec pt >55 °C. Anal. Calcd for $C_{32}H_{68}P_4Pd_2$ (789.6): C, 48.68; H, 8.68; P, 15.69; Pd, 26.95. Found: C, 48.61; H, 8.66; P, 15.83; Pd, 26.95. EI-MS (100 °C): *m/e* (%) 788 (M$^+$, 1), 736 (**12**$^+$, 6), 368 ([(d^{i}ppe)Pd]$^+$, 100). IR (KBr): 3080, 3041 (alkyne and olefinic CH), 1498 (μ-C≡C), 1600 cm^{-1} (noncoordinated C=C). ^{1}H NMR (200 MHz, −80 °C): δ 7.16 (m, 1 H, =CH−), 5.49 [tt, 1 H, ^3J(PH)$_{trans}$ = 18.7 Hz, ^3J(PH)$_{cis}$ = 6.2 Hz, ≡CH], 4.79 [dd, 1 H, ^2J(HH) = 2.0 Hz, ^3J(HH) = 16.5 Hz, =CHH$_Z$], 4.32 [dd, 1 H, ^2J(HH) = 2.0 Hz, ^3J(HH) = 9.4 Hz, =CH$_E$H], alkyne; 1.9 (four unresolved signals, 8 H, PCH), 1.5 (four unresolved signals, 8 H, PCH$_2$), 1.30−0.80 (eight unresolved signals, 48 H, Me), d^{i}ppe. ^{13}C NMR (50.3 MHz, −80 °C): δ 142.7 (m, 1 C, −CH=), 104.1 (m, 1 C, =CH$_2$), 88.5 [tt, 1 C, ^2J(PC)$_{trans}$ = 48.0 Hz, ^2J(PC)$_{cis}$ = 5.2 Hz, ≡C−], 65.5 [m, 1 C, ^2J(PC)$_{trans}$ = 53.2 Hz, ≡CH], alkyne; 26.1 (four unresolved signals, 8 C, PCH), 22.3 (two resolved signals, 4 C, PCH$_2$), 20.9, 19.8, 18.9, 18.5 (each 4 C, Me), d^{i}ppe. ^{31}P NMR (81 MHz, −80 °C): see Table 2.

(d^{i}ppe)Pd(η^2-HC≡CC≡CH) (7c). To the colorless pentane solution (10 mL) of (d^{i}ppe)Pd(C$_2$H$_4$) (794 mg, 2.0 mmol) is added butadiyne (0.35 mL, 5.1 mmol) at −30 °C. At −78 °C off-white microcrystals precipitate, which are isolated as described above and dried at −30 °C under vacuum: yield 780 mg (93%); mp 55 °C dec. Anal. Calcd for $C_{18}H_{34}P_2Pd$ (418.8): C, 51.62; H, 8.18; P, 14.79; Pd, 25.41. Found: C, 51.40; H, 7.87; P, 14.98; Pd, 25.62. EI-MS (70 °C): *m/e* (%) 418 (M$^+$, 2), 368 ([(d^{i}ppe)Pd]$^+$, 56), 50 (C$_4$H$_2$, 100). IR (KBr): 3314 (≡C−H free), 3075 (weak, ≡C−H coord), 2066 (C≡C free), 1690 cm^{-1} (C≡C coord). ^{1}H NMR (400 MHz, −30 °C): δ 7.19 [m, 1 H, ^3J(PH)$_{trans}$ = 31.0 Hz, ^3J(P′H)$_{cis}$ = 21.7 Hz, ≡CH coord], 4.10 [m, 1 H, ^5J(PH) = 4 Hz, ^5J(HH) = 1 Hz, ≡CH free], alkyne; 2.1 (4 H, PCH and P′CH), 1.7 (4 H, PCH$_2$ and P′CH$_2$), 1.21, 1.18, 1.12, 1.03 (each m, 6 H, Me), d^{i}ppe. ^{13}C NMR (75.5 MHz, −30 °C): δ 112.8 [1 C, ^2J(PC)$_{trans}$ = 72.9 Hz, ^2J(P′C)$_{cis}$ = 2.3 Hz, ^1J(CH) = 210 Hz, ≡CH coord], 106.9 [1 C, ^2J(P′C)$_{trans}$ = 66.2 Hz, ≡C− coord], 86.6 [1 C, ^4J(P′C)$_{trans}$ = 7.6 Hz, ^1J(CH) = 249.5 Hz, ≡CH free], 80.7 [1 C, ^3J(P′C)$_{trans}$ = 19.3 Hz, ^3J(PC)$_{cis}$ = 8.1 Hz, ≡C− free], alkyne; 26.0, 25.8

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(each 2 C, PCH and P′CH), 22.8, 22.2 (each 1 C, PCH_2 and $P'CH_2$), 20.2, 20.0, 19.1, 19.0 (each 2 C, Me), d^{i}ppe. ^{31}P NMR (162 MHz, −30 °C): δ 70.2, 68.6 [^2J(PP) = 25 Hz].

{(d^{i}ppe)Pd}$_2${μ-(1,2-η^2):(3,4-η^2)-HC≡CC≡CH} (7d). An ethereal solution (15 mL) of **7c** (419 mg, 1.0 mmol) is added at −78 °C to solid (d^{i}ppe)Pd(η^1-C_3H_5)$_2$ (451 mg, 1.0 mmol). The mixture is warmed to 0 °C for 5 min, and the resulting brown solution is filtered. Over the course of several weeks brown crystals separate at −78 °C, which are isolated as described above and dried under vacuum at −30 °C: yield 640 mg (81%); dec pt >65 °C. Anal. Calcd for $C_{32}H_{66}P_4Pd_2$ (787.6): C, 48.80; H, 8.45; P, 15.73; Pd, 27.02. Found: C, 48.68; H, 8.44; P, 15.65; Pd, 27.15. EI-MS (130 °C): *m*/*e* (%) 786 (M$^+$, <1), 736 (**12**$^+$, 4), 368 ([(d^{i}ppe)Pd]$^+$, 28), 219 ([^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr]$^+$, 100). IR (KBr): see Table 3. ^{1}H NMR (300 MHz, −85 °C; for ≡CH see Table 3): δ 2.0 (8 H, PCH and P′CH), 1.6 (8 H, PCH_2 and $P'CH_2$), 1.2−0.9 (48 H, four unresolved signals, Me), d^{i}ppe. ^{13}C NMR (75.5 MHz, −85 °C; for ≡C− and ≡CH see Table 3): δ 26.2, 25.7 (each d, 4 C, PCH and P′CH), 22.8, 21.9 (each m, 2 C, PCH_2 and $P'CH_2$), 20.4, 18.9 (each d, 8 C, pair of unresolved diastereotopic CH_3), d^{i}ppe. ^{31}P NMR (121.5 MHz, −85 °C): δ 68.0, 64.4 (AA′BB′ spin system).

{(d^{i}ppe)Pd}$_2${μ-(1,2-η^2)-HC≡CC≡CH} (7e). ^{1}H NMR (300 MHz, −85 °C): δ 5.37 [tt, 1 H, $^3J(PH)_{trans}$ = 17.5 Hz, $^3J(PH)_{cis}$ = 7.0 Hz, ≡CH coord], 2.93 [t, 1 H, ^5J(PH) = 3.7 Hz, ≡CH free], alkyne; 2.12 (2 H), 2.03 (2 H), 1.96 (4 H, four kinds of PCH), 1.5 (8 H, PCH_aH_b and $P'CH_aH_b$), 1.25−0.9 (unresolved, 48 H, 8 signals of CH_3 expected), d^{i}ppe. ^{13}C NMR (75.5 MHz, −85 °C; for butadiyne see Table 3): δ 26.0, 25.9, 25.6, 25.4 (each 2 C, four types of PCH), 22.5, 21.5 (each 2 C, PCH_2 and $P'CH_2$), 20.8 (4 C), 20.3 (2 C), 19.4 (4 C), 18.6 (6 C, eight types of CH_3), d^{i}ppe. ^{31}P NMR (121.5 MHz, −85 °C): δ 62.6, 58.7 (AA′BB′ spin system).

(d^{i}ppe)Pt(η^2-HC≡CC≡CH) (7f). To the colorless suspension of Pt(cod)$_2$ (822 mg, 2.0 mmol) and d^{i}ppe (525 mg, 2.0 mmol) in diethyl ether (40 mL) is added at −30 °C butadiyne (0.14 mL, 2.0 mmol). When the mixture is stirred, a burgundy red solution results, from which yellow-orange cubes separate at −78 °C. These are isolated as described above and dried under vacuum at −30 °C: yield 760 mg (75%), dec pt >0 °C. Anal. Calcd for $C_{18}H_{34}P_2Pt$ (507.5): C, 42.59; H, 6.76; P, 12.21; Pt, 38.44. Found: C, 42.92; H, 7.10; P, 12.11; Pt, 38.08. EI-MS (74 °C): *m*/*e* (%) 507 (M$^+$, 40), 457 ([(d^{i}ppe)Pt]$^+$, 100). IR (KBr): see Table 3. ^{1}H NMR (200 MHz, −30 °C; for C_4H_2 signals see Table 3): δ 2.1 (4 H, PCH and P′CH), 1.70, 1.64 (each m, 2 H, PCH_2 and $P'CH_2$), 1.18, 1.10, 1.03, 1.00 (each m, 6 H, Me), d^{i}ppe. ^{13}C NMR (75.5 MHz, −30 °C; for C_4H_2 signals see Table 3): δ 26.6, 26.1 (each 2 C, PCH and P′CH), 24.6, 24.1 (each 1 C, PCH_2 and $P'CH_2$), 19.9, 19.6, 18.9, 18.8 (each 2 C, Me), d^{i}ppe. ^{31}P NMR (121.5 MHz, −30 °C): δ 77.5, 77.2 [$J(PtP_A)$ = 3074 Hz, $J(PtP_B)$ = 3231 Hz, ^2J(PP) = 42.8 Hz].

(d^{i}ppe)Pd(MeC≡CMe) (8a). To a colorless solution of (d^{i}ppe)Pd(C_2H_4) (1.98 g, 5.0 mmol) in pentane (10 mL) is added at 0 °C 2-butyne (1 mL, 12.8 mmol). The resulting light orange solution is cooled to −78 °C, and within 1 day off-white crystals separate which are isolated as described above and dried under vacuum at 0 °C: yield 1.71 g (81%); mp 79 °C. Anal. Calcd for $C_{18}H_{38}P_2Pd$ (422.9): C, 51.13; H, 9.06; P, 14.65; Pd, 25.17. Found: C, 51.10; H, 9.20; P, 14.65; Pd, 24.98. EI-MS (60 °C): *m*/*e* (%) 422 (M$^+$, 11), 368 ([(d^{i}ppe)Pd]$^+$, 100), 54 ([MeC≡CMe]$^+$, 25). IR (KBr): see Table 1. ^{1}H NMR (200 MHz, −80 °C): δ 2.51 (m, 6 H, ≡CMe), 2-butyne; 1.85 (m, 4 H, PCH), 1.67 (m, 4 H, PCH_2), 1.06 (24 H, set of diastereotopic Me), d^{i}ppe. ^{13}C NMR (50.3 MHz, 27 °C): δ 106.6 ("t", 2 C, ≡C−), 16.1 ("t", 2 C, Me), 2-butyne; 26.1 (4 C, PCH), 23.4 (2 C, PCH_2), 20.3, 19.4 (each 6 C, diastereotopic Me), d^{i}ppe. ^{31}P NMR (81 MHz, −80 °C): see Table 2.

{(d^{i}ppe)Pd}$_2$(μ-MeC≡CMe) (8b). A pentane solution (5 mL) of **8a** (423 mg, 1.0 mmol) is combined with a cream-colored suspension of (d^{i}ppe)Pd(η^1-C_3H_5)$_2$ (451 mg, 1.0 mmol) in pentane (10 mL) at −78 °C. When the mixture is warmed to 20 °C, an orange-red solution is obtained from which yellow crystals separate at −30/−78 °C. The product is isolated as described and dried under vacuum at 0 °C: yield 670 mg (85%); mp 80 °C dec. Anal. Calcd for $C_{32}H_{70}P_4Pd_2$ (791.6): C, 48.55; H, 8.91; P, 15.65; Pd, 26.89. Found: C, 48.48; H, 9.12; P, 15.57; Pd, 26.86. EI-MS (100 °C): *m*/*e* (%) 736 (**12**$^+$, 23), 368 ([(d^{i}ppe)Pd]$^+$, 85), 219 ([^{i}Pr$_2$PC$_2$H$_4$P^{i}Pr]$^+$, 88), 54 ([MeC≡CMe]$^+$, 70), 43 (100). IR (KBr): see Table 1. ^{1}H NMR (400 MHz, −30 °C): δ 2.86 (quint, 6 H, ≡CMe), 2-butyne; 1.95 (unresolved, 8 H, PCH), 1.44 (unresolved, 8 H, PCH_2), 1.10, 1.00 (each 24 H, Me), d^{i}ppe. ^{13}C NMR (100.6 MHz, −30 °C): δ 84.9 ("t", 2 C, ≡C−), 18.9 ("d", 2 C, Me), 2-butyne; 26.2, 25.6 (each 4 C, PCH), 23.8 (4 C, PCH_2), 22.5, 22.5, 20.8, 20.0 (each 6 C, diastereotopic Me), d^{i}ppe. ^{31}P NMR (162 MHz, −30 °C): see Table 2.

(d^{i}ppe)Pd(PhC≡CPh) (9). To a colorless solution of (d^{i}ppe)Pd(C_2H_4) (397 mg, 1.0 mmol) in diethyl ether (5 mL) is added an ethereal solution (5 mL) of PhC≡CPh (210 mg, 1.2 mmol) at 20 °C. Colorless crystals precipitate, which are isolated as described (−30 °C) and dried under vacuum (20 °C): yield 755 mg (87%); mp 166 °C. Anal. Calcd for $C_{28}H_{42}P_2Pd$ (547.0): C, 61.48; H, 7.74; P, 11.32; Pd, 19.45. Found: C, 61.39; H, 7.65; P, 11.42; Pd, 19.46. EI-MS (95 °C): *m*/*e* (%) 546 (M$^+$, 10), 368 ([(d^{i}ppe)Pd]$^+$, 100), 178 ([C_2Ph_2]$^+$, 83). IR (KBr): see Table 1. ^{1}H NMR (400 MHz, 27 °C): δ 7.60 (4 H), 7.22 (4 H), 7.04 (2 H), C_2Ph_2; 2.13 (m, 4 H, PCH), 1.68 (m, 4 H, PCH_2), 1.12, 1.05 (each m, 12 H, diastereotopic Me), d^{i}ppe. ^{13}C NMR (100.6 MHz, 27 °C): δ 138.2 (2 C, C_α), 130.2 (4 C, C_β), 128.3 (4 C, C_γ), 125.5 (2 C, C_δ), 126.1 (2 C, ≡C−), C_2Ph_2; 26.8 [4 C, ^1J(PC) = 7.6 Hz, PCH], 22.8 ["t", 2 C, ^1J(PC) ≈ ^2J(PC) ≈ 18.1 Hz, PCH_2], 20.5, 19.0 (each 4 C, diastereotopic Me), d^{i}ppe. ^{31}P NMR (162 MHz, 27 °C): see Table 2.

(d^{i}ppe)Pd(MeO$_2$CC≡CCO$_2$Me) (10). To a solution of (d^{i}ppe)Pd(C_2H_4) (791 mg, 2.0 mmol) in diethyl ether (10 mL) is added at 0 °C an ethereal solution (10 mL) of MeO_2-CC≡CCO_2Me (0.5 mL, 4.1 mmol). Colorless crystals form, which are isolated as described above and dried under vacuum (20 °C): yield 920 mg (90%); mp 101 °C. Anal. Calcd for $C_{20}H_{38}O_4P_2Pd$ (510.9): C, 47.02; H, 7.50; O, 12.53; P, 12.13; Pd, 20.83. Found: C, 47.09; H, 7.46; P, 11.98; Pd, 20.71. EI-MS (90 °C): *m*/*e* (%) 510 (M$^+$, 4), 368 ([(d^{i}ppe)Pd]$^+$, 100). IR (KBr): 1679, ∼1190 cm^{-1} (CO_2Me); for alkyne ligand, see Table 1. ^{1}H NMR (400 MHz, 27 °C): δ 3.64 (s, 6 H, CO_2Me), alkyne; 2.06 (m, 4 H, PCH), 1.78 (m, 4 H, PCH_2), 1.14, 1.07 (each 12 H, diastereotopic Me), d^{i}ppe. ^{13}C NMR (100.6 MHz, 27 °C): δ 167.9 (2 C, *C*O_2Me), 122.7 (2 C, ≡C−), 51.1 (2 C, CO_2*Me*), alkyne; 25.9 (4 C, PCH), 22.9 [2 C, ^1J(PC) = 20 Hz, ^2J(PC) = 17 Hz, PCH_2], 19.9, 19.3 (each 4 C, diastereotopic Me), d^{i}ppe. ^{31}P NMR (162 MHz, 27 °C): see Table 2.

(d^{i}ppe)Pd(Me$_3$SiC≡CSiMe$_3$) (11). To the colorless solution of (d^{i}ppe)Pd(C_2H_4) (794 mg, 2.0 mmol) in diethyl ether (5 mL) is added Me_3SiC≡$CSiMe_3$ (0.5 mL, 2.2 mmol) at 20 °C. When the solution is cooled to −78 °C (1 day), off-white cubes crystallize, which are separated as described above and dried under vacuum at 20 °C: yield 850 mg (79%); mp 50 °C dec. Anal. Calcd for $C_{22}H_{50}P_2PdSi_2$ (539.2): C, 49.01; H, 9.35; P, 11.49; Pd, 19.74; Si, 10.42. Found: C, 48.75; H, 9.28; P, 11.41; Pd, 19.92; Si, 10.55. EI-MS (40 °C): *m*/*e* (%) 538 (M$^+$, 8), 368 ([(d^{i}ppe)Pd]$^+$, 100), 170 ([C_2(SiMe$_3$)$_2$]$^+$, 4). IR (KBr): 1239, 861/36 ($SiMe_3$); for alkyne ligand, see Table 1. ^{1}H NMR (200 MHz, 27 °C): δ 0.22 (s, 18 H, $SiMe_3$), alkyne; 2.04 (m, 4 H, PCH), 1.65 (m, 4 H, PCH_2), 1.08, 1.07 (each m, 12 H, diastereotopic Me), d^{i}ppe. ^{13}C NMR (50.3 MHz, 27 °C): δ 134.7 ["t", 2 C, $^2J(PC)_{trans} \approx {}^2J(PC)_{cis} \approx$ 20 Hz, C≡C], 2.3 (6 C, $SiMe_3$), alkyne; 27.2 [4 C, ^1J(PC) = 6.5 Hz, PCH], 23.4 ["t", 2 C, ^1J(PC) ≈ ^2J(P′C) ≈ 18 Hz, PCH_2], 21.4, 19.3 (each 4 C, diastereotopic Me), d^{i}ppe. ^{31}P NMR (81 MHz, 27 °C): δ 63.4 [^3J(SiP) = 16 Hz].

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Supporting Information Available: Tables of data collection information, anisotropic thermal parameters, atom coordinates and *U* values, and bond lengths and angles for **3a** (4 pages). Ordering information is given on any current masthead page.

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